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Review

The role of photoinduced electron transfer in the quenching of sensitized Europium emission

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ABSTRACT

Lanthanide (Ln) complexes equipped with a light-harvesting antenna can undergo numerous processes upon light excitation of the chromophore. Some of these, e.g., energy transfer to the Ln are beneficial for Ln luminescence, while others, e.g., interactions with O—H oscillators, are detrimental. Eu(III) is the most reducible of the Ln(III) ions, with a reduction potential of *E*(Ln(II)/Ln(III)) = −0.35 V vs NHE for the hydrated ions. This means that the Eu(II) redox state is relatively easily accessible by reduction with a range of excited state aromatics, such as are present in luminescent Ln complexes carrying a light-harvesting antenna. Electron transfer almost always results in diminished Eu emission quantum yields, and is therefore undesirable; however, it is usually not taken into consideration during complex design. Here, we evaluate the role of Eu complex design for electron transfer. We also discuss strategies for diminishing this quenching pathway, including lowering the reducing power of the antenna excited state, and increasing the stability of the +3 oxidation state of Eu. Finally, we review applications of Eu(II) and photoexcited Eu(II).

Contents

1. Introduction

The luminescence of trivalent lanthanides (Ln(III)) is exploited in areas as diverse as in vitro and in vivo luminescent bioprobes [1–7], telecommunications [8] and anti-counterfeiting technologies [9]. The vast majority of the bioprobes are based on Eu and Tb, as these ions have the highest intrinsic quantum yields [3,4,6,7,10,11]. Ln(III) emission is due to f–f transitions [12]. As a consequence, emissions are long-lived, with in some cases up to ms lifetimes; this is to be compared with the ns timescale of organic emitters. The emission peaks are sharp, and their positions

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Abbreviations: PeT, photoinduced electron transfer; Ln, lanthanide; ET, energy transfer; BET, back energy transfer; ISC, intersystem crossing; Ant, antenna; NIR, near infrared; tta, thenoyltrifluoroacetonate; dbpt, 2-(N,N-diethylanilin-4-yl)-4,6-bis(3,5)-dimethylpyrazol-1-yl)-1,3-5-triazine; LMCT, ligand to metal charge transfer; fod, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctadienone-3,5; DTPA, diethylenetriaminepentaacetic acid; DOTA, 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid; τ_{H2O}, luminescence lifetime in water; τ_{D2O}, luminescence lifetime in D_2O; Q, external quencher; *q*, number of Ln-bound water molecules.

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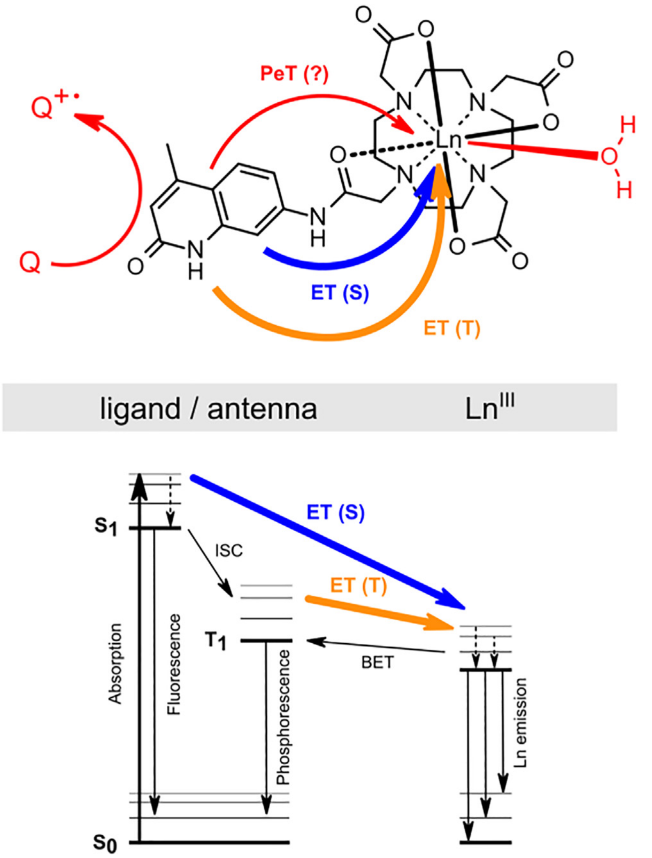

Fig. 1. Ln luminescence sensitization by a light-harvesting antenna in a typical multidentate chelate framework. The energy transfer and quenching pathways are shown (top). Energy diagram of the Ln sensitization (bottom).

are specific for the metal ion, largely unaffected by the coordination environment. The forbidden nature of these transitions means that direct excitation is inefficient. This problem is often circumnavigated by the installation of a light-harvesting antenna into the proximity of the metal ion [12]. Energy transfer from the antenna to the Ln(III) produces excited Ln(III)*, which can relax with the emission of a photon characteristic of the metal (Fig. 1).

A large body of work discusses the requirements for a good sensitizing antenna [13]. The parameters usually considered most important are the antenna's excited singlet and triplet levels and its distance from the metal ion [13]. Often energy transfer (ET) from the antenna triplet state is assumed [14]. As a general rule, for fast ET the triplet should be not more than 5000 cm^{-1} above the Ln(III) receiving level (17,200 cm^{-1} for Eu, 20,400 cm^{-1} for Tb [15] and 10,300 cm^{-1} for Yb [16]). To avoid energy back transfer the Ln must be at least $10k_BT$ above the antenna triplet (i.e., 2000 cm^{-1} at room temperature). ET from the antenna singlet excited state has been considered less important despite suggestions early on that it was a viable process [17,18]. This has changed in the past decade with an increasing number of lanthanide complexes for which singlet energy transfer has been shown to contribute to sensitization [19–21]. There is a third well-established sensitization pathway available for Yb, based on stepwise electron transfer from the excited antenna to the Yb(III), and back electron transfer (*vide infra*) [16,22–25].

The Ln(III) and the antenna are typically linked by multidentate ligands, often based on cyclen (1,4,7,10-tetraazacyclododecane) and nonane (1,4,7-triazacyclononane) macrocycles. The thermodynamic and kinetic stabilities of their emitters are key for emitters destined for biological use [26,27]. In addition to preventing the metal ion from leaching, such ligands also shield the metal from quenching O—H and N—H oscillators [28–30]. Protection from C—H oscillators is less crucial in Eu and Tb complexes, but it becomes important for near infrared (NIR) emitters, such as Yb, Nd and Er [29]. For this latter group, ligand deuteration can measurably reduce quenching attributable to C—H oscillators [31–33], although there are exceptions [34]. Even subtle changes in ligand bulk can have dramatic effects, as shown by the replacement of carboxylate donors with monophosphonate ones. The larger phosphonate monoesters shield the metal more efficiently than the carboxylate, which manifests itself in fewer coordinated water molecules (q) [35,36]. In summary, when these parameters are optimized, emitters with high quantum yields, and what is even more important for bioimaging, high brightness ($B = A^*\Phi$) can be obtained [27,37–40].

In this review, we discuss a quenching mechanism that usually goes undetected, and, based on the reviewed literature, is not taken into consideration during emitter design. We argue that quenching by photoinduced electron transfer (PeT) is a potentially important contributor for diminished Eu luminescence, and there are large benefits to be gained by shutting it down. We go on to suggest two strategies for decreasing its impact. Finally, we provide an overview of the so far scarce synthetic use of the Eu(II) complexes.

We note that PeT has been invoked in different contexts in Ln complexes. Intraligand electron transfer has been observed in anthracene-sensitized Ln complexes wherein a dimiine ligand is coordinated to the Ln. In these systems electron transfer did not involve the metal, and took place even when the redox-active Ln was replaced by Gd(III), Zn(II) or H^+ [41]. A large number of responsive probes are based on the principle of PeT quenching of the antenna excited state by an external quencher (e.g., cellular reductants) or a proximal amine [2,42–44]. These systems will not be discussed here.

2. Effect of PeT on Ln luminescence

Electron transfer from the excited antenna to the Ln(III) can have different downstream effects depending on the Ln. PeT is the first step of an Yb(III) sensitization mechanism (Fig. 2) [16]. This mechanism is distinct from Dexter energy transfer, which consists of simultaneous electron transfers. Yb emission is obtained in systems equipped with antennae that have diminutive spectral overlap with the near infrared-emitting Yb. The proposed mechanism, which has been investigated in depth [22,25,41,45], is based on the formation of a high-energy intermediate state, Yb(II)/$Ant^{+\cdot}$. If this state is more energetic than Yb(III)* electron back transfer yields Yb(III)* which can relax by emitting a NIR photon [16]. For other Lns, the receiving levels are much higher in energy, and the Ln(II)/$Ant^{+\cdot}$ intermediate is usually below this level (Fig. 2). Thus,

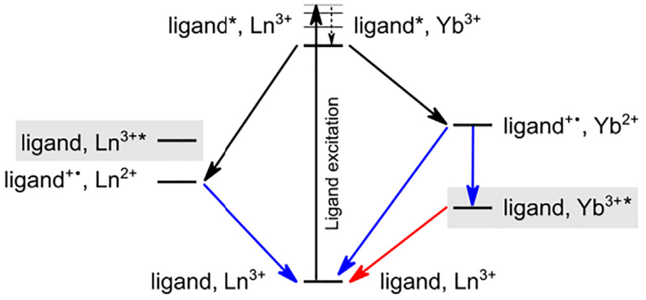

Fig. 2. The effect of ligand-to-Ln electron transfer in Yb, which has a low-lying excited state (right), and other easy to reduce Ln(III) ions with high-energy excited states (left). Black arrows: electron transfer, blue arrows: back electron transfer, red arrow: radiative decay.

PeT is typically quenching for non-Yb emitters. A notable exception is Eu(tta)$_2$dpbt (tta = thenoyltrifluoroacetonate, dbpt = 2-(N,N-diethylanilin-4-yl)-4,6-bis(3,5)-dimethylpyrazol-1-yl)-1,3-5-triazine) [46]. The decay of the dbpt ligand fluorescence in this complex could be monitored by time-resolved spectroscopy. The faster decay component was attributed to population of the LMCT state, while the slower one was shown to be due to delayed fluorescence caused by energy back transfer from the LMCT state to the ligand singlet excited state. The LMCT state was funnelling the excitation energy into the $^5D_1$ Eu(III) receiving level [46]. The Eu(2.2.1) cryptand, which lacks an organic chromophore can be excited into the metal-centered Eu(III) $^5L_6$ band (393 nm), as well as into charge transfer bands at 260 and 350 nm, even though the latter is only about 3–10% as efficient as the direct excitation [47].

A range of antenna/Eu(III) combinations have been found to have low emission quantum yields due to PeT quenching. Fluorescent aromatic hydrocarbons, including perylene, anthracene and electron-poor 1,2,9,10-tetracyanoanthracene are quenched by Eu(III) and Yb(III) by intermolecular electron transfer [48]. The modest efficiency of the 2,2′-bipyridine antenna in **1a** and **1b** was suggested to be due to ligand-to-metal electron transfer. In both systems it was suggested that the charge transfer state decays rapidly to the ground state [49,50]. The dramatic quenching of emission quantum yields by LMCT in Eu(bipy)$_3$-type complexes states could be quantified by theoretical models [51], along with the transfer rates [52]. The role of complex geometry for electron transfer is highlighted by the differences seen in 1:1 and triple helical 3:1 Eu complexes of terpyridine-like **2**. The LMCT state was lower in energy in the cage-like 3:1 complexes, which resulted in a dramatic drop in Eu emission due to increased PeT [53]. Interestingly, cyclic voltammetry could explicitly rule out PeT in Eu complexes of 2,2′:6′,2″-terpyridines substituted in the 4-positions with ethyl and *tert*-butyl groups [54]. The Eu emission of **3** was completely quenched at high pH (Chart 1). Deprotonation of the OH-group increased the electron density on the antenna making PeT to the Ln favorable [55]. The excited state of tryptophan is a competent electron donor to Eu(III). This has been exploited in the investigation of protein structure, whereby spectroscopically silent and redox inactive Ca(II) was replaced by Eu(III) (or Yb(III)) to reveal the number and position of the metal binding sites [56,57]. While PeT is also possible from tryptophan to Eu(fod)$_3$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctadienone-3,5), the acceptor here is the organic ligand rather than the Eu(III) [58]. Diketonates are among the most studied ligands for Lns, acting both as the metal binder and the sensitizing antenna. Electronically diverse diketonates (**4a**–**d**) undergo deactivation via a LMCT state [59,60], as does their extended analog **4e** in the Eu$_2$[**4e**]$_3$ complex [61].

To assess the scope of Lns susceptible to PeT, the driving force for Ln(II) formation must be calculated. This can be done using the Rehm–Weller equation (Eq. (1)), where $E^{ox}_{1/2}$ and $E^{red}_{1/2}$ are the oxidation and reduction potentials of the donor (i.e., antenna) and the acceptor (Ln(III)), respectively. $E_{exc}(D)$ is the excited state energy of the antenna. The ΔE_{Coul} term is the attraction between the radical ion pair that is the product of PeT [62].

$$\Delta E = E^{ox}_{1/2}(D) - E^{red}_{1/2}(A) - E_{exc}(D) - \Delta E_{Coul} \tag{1}$$

Taking the Ln(II)/Ln(III) redox potentials of the aquo ions [63,64], one can determine the driving force for a given excited antenna–Ln(III) pair. Alternatively, one can estimate the lowest oxidation potential for an antenna for which PeT will not be possible at a given excited state (Fig. 3). These results suggest that for most common organic antennae, PeT should be feasible for Yb and Eu. The surprising outcome of this analysis is that even for other, more difficult to reduce Ln(III) ions, such as Sm, Dy, Tm, and possibly Nd, PeT should be considered. These results question a very general assumption about the behavior of Ln(III) in luminescent complexes, namely that, with the exception of Yb and Eu, they are exclusively in the stable +3 oxidation state. These assumptions are somewhat justified. First, as noted above, ET and PeT are competing processes, and if ET outcompetes PeT, Ln(II) formation is not relevant. Second, Ln(II)/Ln(III) redox potentials vary considerably with the ligand, and the values determined for the aquo ions can be shifted by several hundreds of mV upon Ln complexation (*vide infra*). Third, PeT contribution may go unnoticed next to those of other quenching mechanisms. A decrease in antennae residual fluorescence in Eu complexes is a likely indication that PeT may be

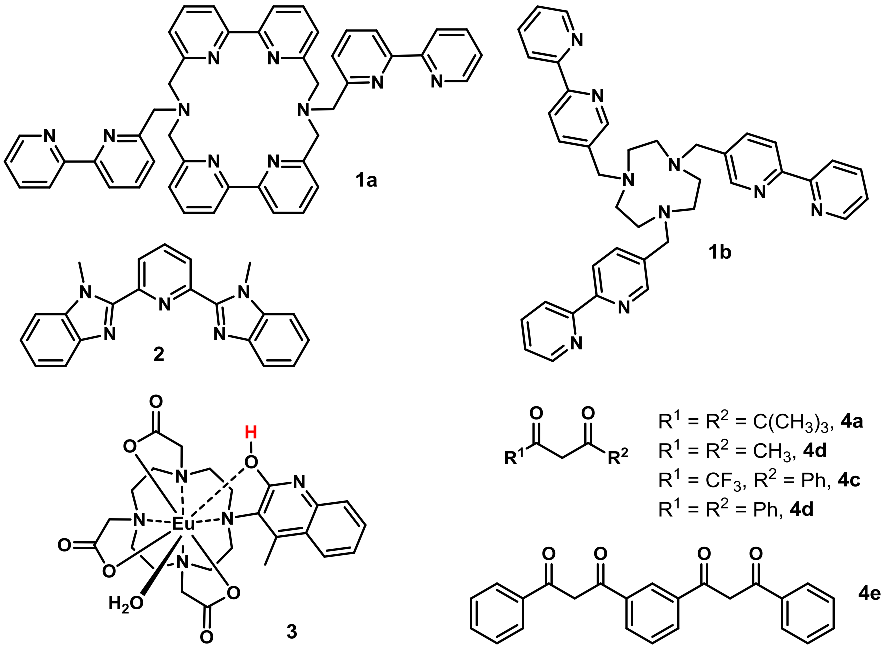

Chart 1.

occurring. However, other reasons, such as singlet-mediated energy transfer may have the same effect, which makes the unambiguous identification of PeT quenching difficult.

Diphenylamine fluorescence was quenched by a range of Ln(III) ions (Eu, Yb, Sm, Nd, Dy, Pr, Ho, Er, Tb and Gd); PeT was suggested to take place in all cases. However, the free energies for PeT for at least three of these ions (Gd, Tb and Er) are >0 eV, and the bimolecular quenching constants did not correlate with the calculated free energies. Therefore, additional processes must contribute to the observed results [65].

A structure-photophysics study of 6 oxycoumarin, 2 amidocoumarin and 6 carbostyril antennae in combination with multiple Lns (Eu, Tb, and Gd for coumarins; Eu, Tb, Sm, Dy, Nd, Yb and Gd for carbostyrils) revealed that singlet-mediated ET was significant for those oxycoumarin antennae which were attached by a relatively long triazole linker. For this group of complexes PeT did not seem to be prominent, and residual fluorescence of the antenna was only diminished due to ET. For the carbostyrils however, which were directly coordinated to the Lns, both PeT and ET from the singlet were feasible as shown by cyclic voltammetry (**5a**–**f**, Chart 2). The individual contributions of PeT and ET could be estimated. Yb has only one low-lying excited state at 10,300 cm^{-1}, and is therefore unlikely to participate in singlet-mediated sensitization. Tb(III) on the other hand is extremely stable (Table 1), and PeT from the antenna to the Ln(III) could be excluded in all its studied complexes. Gd(III) is both hard to reduce and unable to act as an energy acceptor. These three ions were used as anchor points. It was found that in this set of complexes, both ET and PeT are relevant for Eu, Sm, Dy and Nd, with ET contributing to increased Ln emission and PeT diminishing it (Fig. 4) [21].

3. Ways to control PeT

3.1. Ln–antenna distance

PeT and ET are competing processes with different distance dependences. This has been seen in the oxycoumarin and carbostyril systems, wherein the longer linker of the coumarins stopped PeT [21]. In theory it should be possible to optimize the antenna–Ln distance to minimize PeT and maximize ET *relative to each other*. However, increasing the Ln–antenna distance will also diminish the ET efficiency, therefore the benefits of such an approach are questionable.

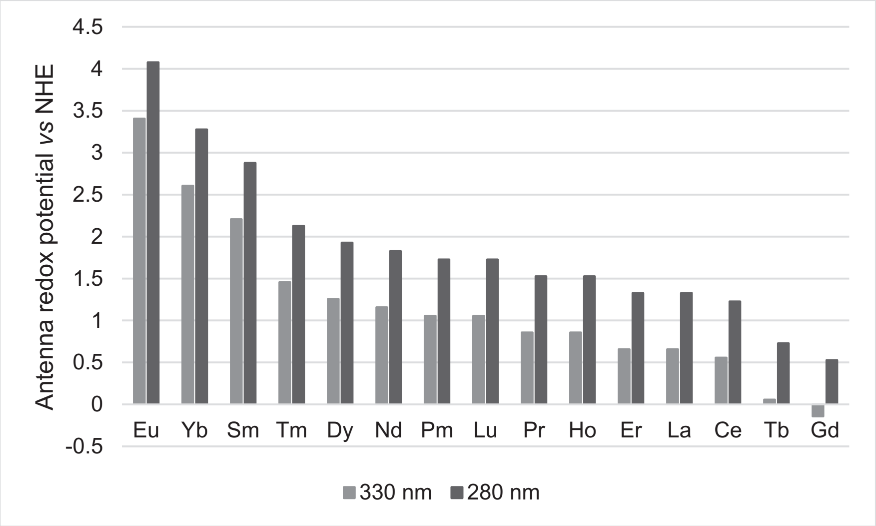

Fig. 3. Antenna redox potentials below which PeT to Ln(III) ions is unfavorable upon 280 nm or 330 nm excitation.

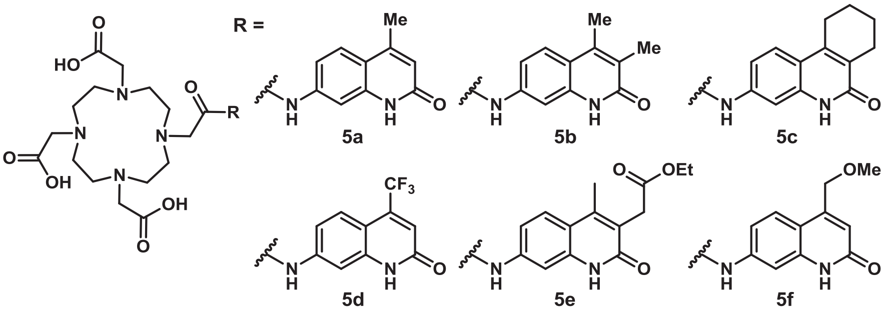

Chart 2.

Table 1
Ln(II)/(III) redox potentials vs NHE [63,64].

Gd	Tb	Ce	La	Er	Ho	Pr	Lu	Pm	Nd	Dy	Tm	Sm	Yb	Eu
−3.9	−3.7	−3.2	−3.1	−3.1	−2.9	−2.9	−2.7	−2.7	−2.6	−2.5	−2.3	−1.55	−1.15	−0.35

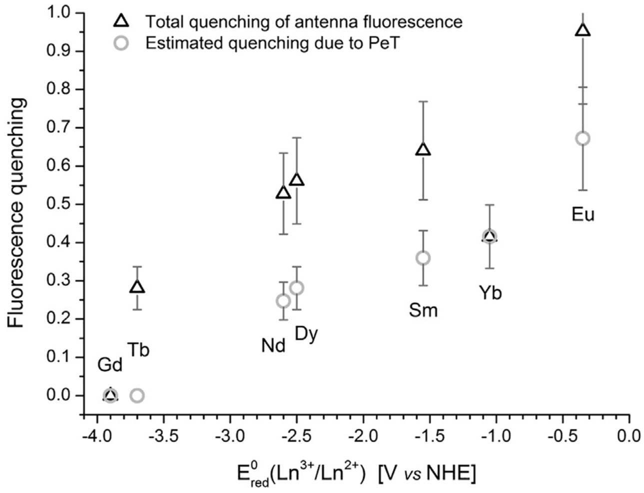

Fig. 4. Estimating the contributions of singlet-mediated energy transfer and PeT to the decrease in antenna residual fluorescence in DOTA-type **5a–f** complexes. Adapted from Ref [21].

3.2. Antenna redox properties

The driving force for PeT can be decreased by lowering the excited antenna reducing power through withdrawing electron density from the antenna. The simplest way to do this is by protonation of a basic nitrogen in the chromophore. At pH ~6.5–7 phenanthridine is essentially unprotonated, while the protonated form dominates at pH 1.5–2.5. The overall charge neutral phenanthridine-appended **Eu6** increased its luminescence quantum yield from 1.1% to ~3% upon protonation to **Eu6**H$^+$. The analogous triamide **Eu7** with a +3 overall charge showed a similar increase, from $\Phi_{Ln} = 0.4\%$ to $\Phi_{Ln} = 2.2\%$ upon protonation to **Eu7**H$^+$. Both of these changes can be ascribed to a decreased PeT quenching. When the Tb complexes of the same ligands were protonated, the Ln luminescence quantum yields decreased [66]. This highlights a potential problem with decreasing PeT quenching via changing the antenna electronics, namely, the lowering of the antennae reducing power is accompanied by a change in the antenna excited state energy. This in turn alters the energy transfer rate, or can render new detrimental processes viable. In the above case, protonation lowered the phenanthridine triplet by ~800 cm^{-1} to within 2000 cm^{-1} of the Tb(III) excited state, making thermal energy back transfer to the antenna triplet possible [67]. The repopulated antenna triplet is susceptible to quenching by atmospheric oxygen, which decreases the overall Tb quantum yield.

Similarly, the Eu(III) complex of **5a** and its analog wherein the methyl group is replaced by a trifluoromethyl group (**5d**) can be compared (Chart 3). Again, withdrawing electrons from the antenna decreases its reducing power, which increases the Eu (III)-centered emission from 3.1% in **5a** to 7.9% in **5d** (Chart 1) [21]. However, as in the previous example, the Tb complex emission suffers, in this case dropping quite dramatically, from 35% in **Tb5a** to 3% in **Tb5d**. The reason is the same as in the **Ln6**/**Ln6**H$^+$ and **Ln7**/**Ln7**H$^+$ systems, the antenna triplet in **5a** is at 23,500 cm^{-1} while in **5d** it is at 22,400 cm^{-1}.

3.3. Ln redox properties

The Ln(III)/Ln(II) redox potential is dependent on the metal environment. *E*(Eu(III)/Eu(II)) differs by ~1 V in DMSO and acetonitrile [68], replacing water with an ionic liquid has an only slightly smaller effect [69].

The first systematic studies on ligand effect on Eu redox potential were done on cryptates [47,68,70,71]. These efforts intensified with the discovery that Eu(II) complexes could act as environment-sensitive MRI contrast agents [72–76]. Weaver and co-workers observed that the Eu(2:2:1) cryptate redox potential shifted to more negative values upon the addition of hydroxide or fluoride ions, proving that the anions could bind to the encapsulated Eu (III) [70]. Eu(III) in the larger 2:2:2 cryptate was even more reducible, as was a Eu(2:2:1)-analog wherein one of the aliphatic —O(CH$_2$CH$_2$)O— units was replaced by a catechol [71]. Allen has varied the electron-withdrawing ability of the catechol by adding a 3-F substituent, as well as the Lewis basicity of the donor atoms by exchanging the ethers with thioethers [77]. Both fluorination and increased donor atom basicity stabilized the Eu(II) oxidation state, the latter parameter was the more influential [77]. It is important to note that the above-mentioned solvent effects were observed even for fully-encapsulated 2:2:2 and 2:2:1 cryptands of Eu, Yb and Sm, albeit to a smaller extent [68]. The importance of this finding is that even Lns complexed in multidentate ligands are sensitive to small changes in the environment, which makes approximations of Ln redox couples highly uncertain.

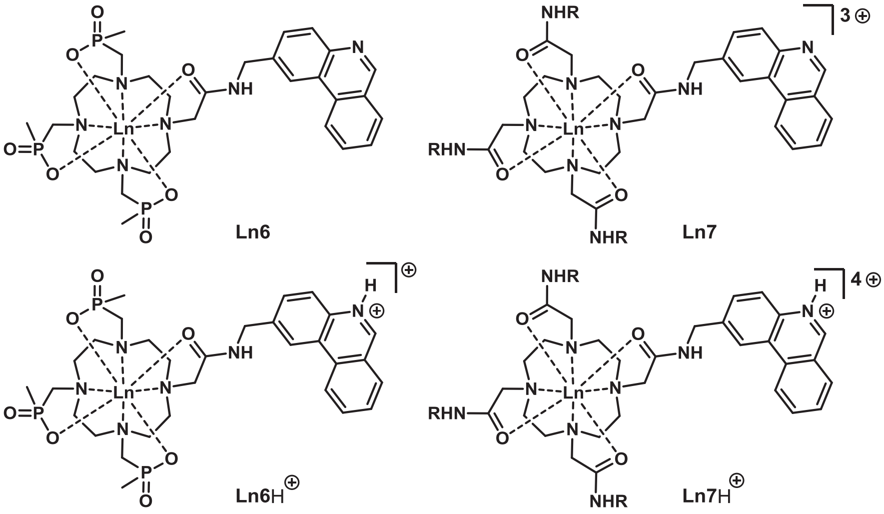

Chart 3.

The majority of luminescent Ln complexes are based on polyaminocarboxylates (Fig. 5). Several linear polyaminocarboxylates were found to stabilize the Eu(III) redox state compared to the aquo ions. The most negative redox potential was observed for the −6 charged ttha ligand (**8**) [78]. The macrocyclic ligands **19** and **20** with two and one negative charges, respectively, shift the Eu(III)/Eu(II) redox potential to more negative values than that of the hydrated ion, while uncharged **21** (which yields a +3 charged complex) stabilizes the Eu(II) compared to Eu^{3+}(aq) [79,80].

In summary, while precise prediction of the Eu redox potential in a chelate is not yet possible, there are a number of factors that are known to shift it to more negative values. For macrocyclic complexes and cryptates smaller ring and cavity sizes stabilize the smaller Eu(III). For both cyclic and linear ligands, an increasing electron density on the metal has the same effect.

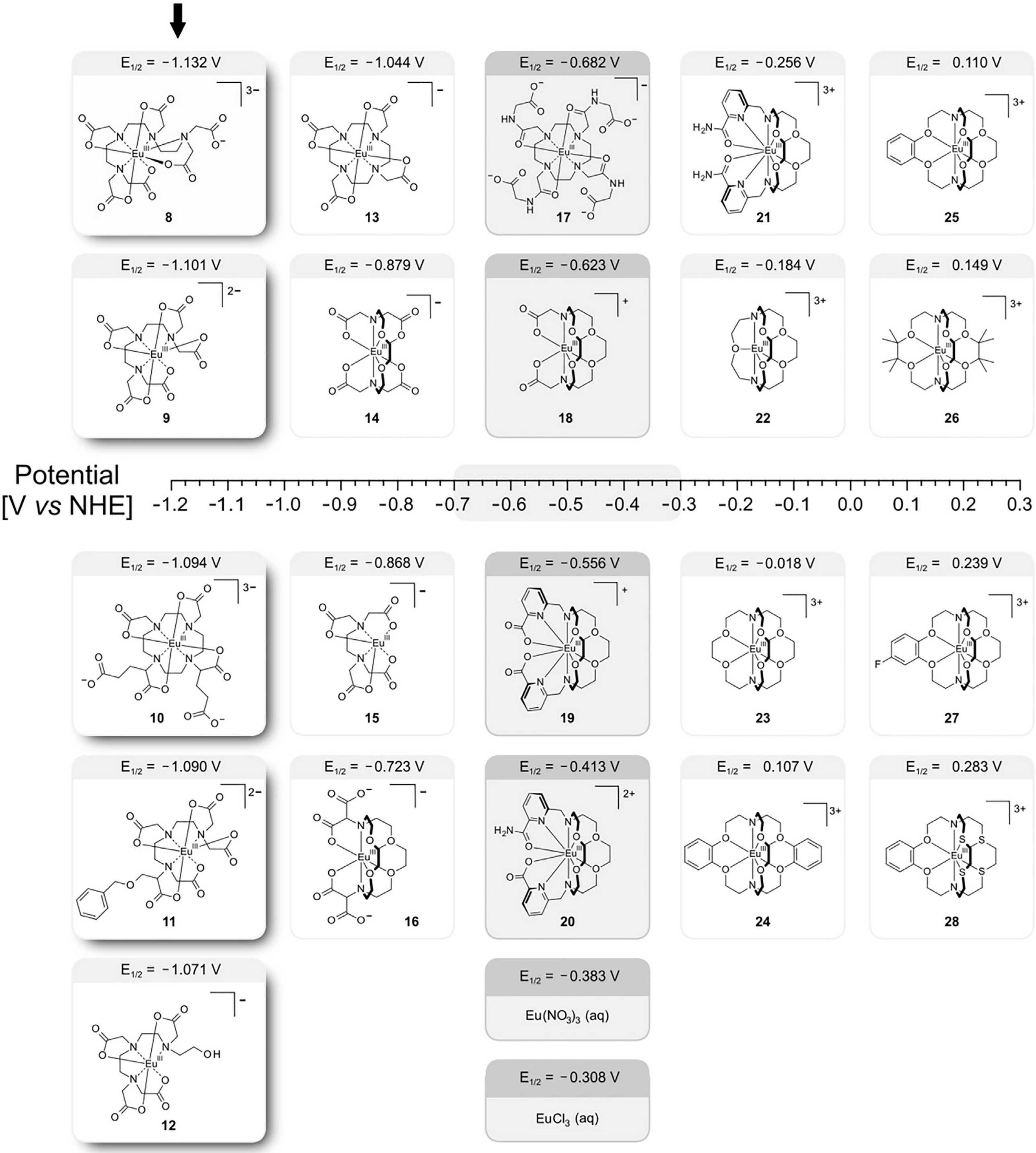

Fig. 5. Eu(II)/Eu(III) redox potentials of common complexes with multidentate ligands. Potentials were converted to NHE from the original data to enable comparison. The gray scale indicates the middle of the range. The arrow points to the first column, potentials increase from top to bottom. The effect of supporting electrolyte concentration and pH were determined in some cases and were found to be small (<50 mV) [78]. Compounds **8**, **9**, **11**, **12**, **14**, **15** are from [78], **9**, **16**, **18** from [81], **9**, **10**, **13** from [82], **16**, **18**, **19**, **20**, **21** from [79], **17**, $EuCl_3$, **27** from [83], $Eu(NO_3)_3$, **23**, **24**, **25**, **26**, **27**, **28** from [77], and **22** and **23** from [71].

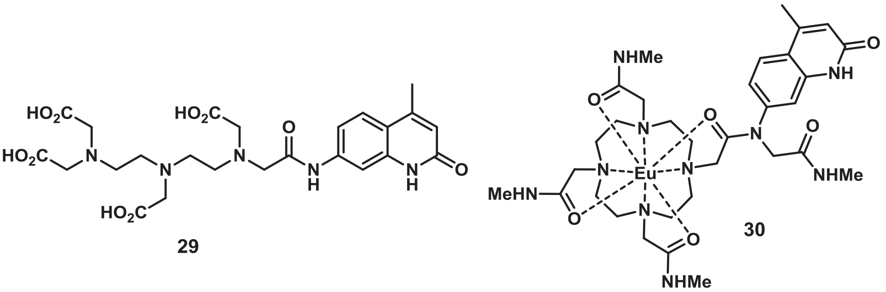

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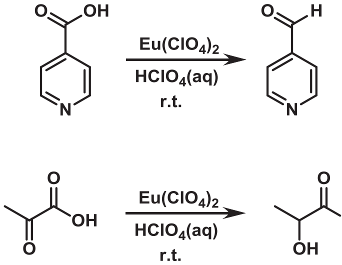
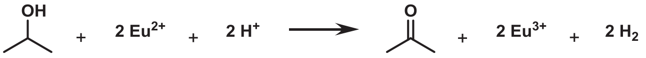
Chart 4.



Scheme 1.



Scheme 2.

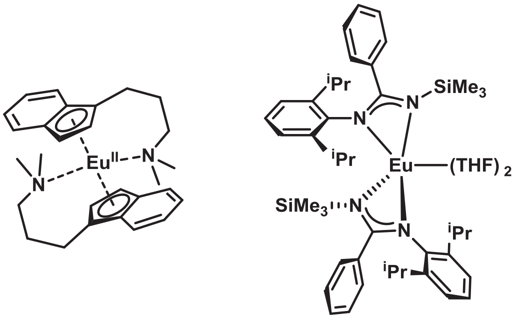


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Chart 5.

The effect of ligand on the Eu(III)/Eu(II) redox potential is thus substantial. With PeT quenching in mind, stabilization of Eu(III) should increase the Eu(III) luminescence. An evaluation of this parameter requires attaching the same antenna with the same linker (functional group and length) to Eu chelates with different redox potentials. To enable comparison, not only the antenna-Eu distance, but also the hydration state (*q*) of the metal has to be kept constant. A decrease in PeT under such strictly controlled conditions may be observable in two ways: (a) as an increase in Eu-emission (Φ_{Ln}), and (b) as an increased antenna residual fluorescence quantum yield (Φ_L).

There are a handful of examples in the literature which enable the correlation of changing Eu redox potential with a change of Ln luminescence. One of the most widely used antennae is 4-methylcarbostyril (cs124). It has been suggested that the excited cs124 amide antenna is a suitable PeT donor for Eu(III) [84], this has been confirmed by cyclic voltammetry on a model compound [21]. Selvin and Xiao have prepared the Eu(III) complexes of DTPA (**29**, Chart 4) and DOTA (**5a**) ligands [85]. The Eu luminescence quantum yields were 9.9% and 5.7%, respectively. In both complexes the amide linker is presumably coordinated to the Eu. The complexes have identical hydration states (same τ_{H2O} and τ_{D2O} within experimental error), therefore the differences are not ascribable to differences in *q* or Ln–antenna distance. The most obvious explanation for the quantum yield difference is the different Eu redox potentials in the chelates. **Eu5a** is charge neutral, while **Eu29** has an overall negative charge, which destabilizes Eu (II), thus increasing Eu(III) emission. Interestingly, a +3-charged Eu complex of the triamide analog (**30**, Chart 4) is an even poorer emitter than **Eu5a**, with Φ_{Ln} = 1.4%, although some of this may be due to the slight change in the antenna structure [84]. Further support for PeT as an explanation for the observed results comes from the Tb complexes of the same two ligands. These have identical quantum yields within experimental error (32.4% and 32.0% for **Tb29** and **Tb5a**, respectively), as would be expected for complexes lacking a redox-active metal wherein all other sensitization and quenching contributions are alike [85].

In another example, the neutral phenanthridine complex **Eu6** (Chart 4), while only has a Φ_{Ln} = 1.1%, is still more emissive than its +3 charged analog **Eu7**. Again, the most important difference between these two complexes is the chelate structure, and thus the Eu redox potential [66].

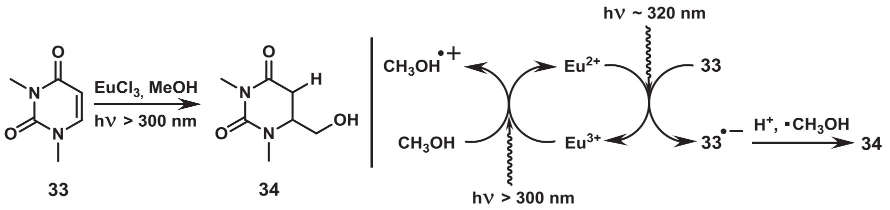
A limitation of this approach to reducing PeT is that the bulk of the research on Eu(II)/Eu(III) redox potential modulations was carried out with the purpose of turning Eu(II) complexes into MRI contrast agents. The studied ligands aim to stabilize the +2 oxidation state, which is to be avoided in luminescent complexes.

4. The utility of Eu(II) in organic synthesis

Divalent Lns are single electron reductants. The most widely used Ln(II) compound in organic synthesis is SmI_2. In the solid state SmI_2 has been known for more than 100 years, but the solution synthesis and isolation of divalent lanthanide ions in their molecular complexes started in the second part of the 20th century (1960s) [86]. The first examples of isolated Ln(II) complexes were the ones containing Lns with more positive reduction potentials (i.e., Eu, Yb, Sm) (see Table 1). Since then, Ln(II) complexes for the whole Ln series have been isolated [87].

From a practical point of view Sm(II) is the best reducing agent. Its reduction potential is negative enough to reduce many functionalities (aldehydes, ketones, alkyl halides), however, it is stable enough to be kept in solution for an extended period of time. After the introduction of SmI_2(thf) by Kagan in 1977, this reagent became widely used in natural product total syntheses [88].

Eu(II) has the lowest reducing ability among all Lns. Different ligands (complexation environment), counterions, solvents and photoirradiation alter the Sm(II) redox potential, often yielding more reducing species [89]. In the past 20 years the same strategy



Scheme 3.

has been used to change the reducing ability of Eu(II), usually in order to stabilize the reduced form for in vivo MRI applications [83,90].

Since Eu(II) is a weak reductant, its usage in organic synthesis is scarce. There are only a few examples where Eu(II) was used under mild conditions without photoexcitation. One of the first reductions was performed by Katakis and co-workers, who successfully reduced carboxylic acids and ketones in acidic aqueous solutions. However, these functionalities were only reducible by Eu(II) in activated positions [91–93] (Scheme 1). The proposed reaction mechanism contains two separate single-electron-transfer steps mediated by Eu(II). Several N-containing electron-poor heterocycles (pyridines, quinoxolines) were competent electron acceptors under these conditions [94].

Single electron transfer from metals to an organic monomer can start radical chain reactions. The organometallic sandwich-type Eu(II) complex (**31**) proved to be a good initiator in polymethyl methacrylate polymerizations (Chart 5) [95]. The neutral, mononuclear Ln(II) formed with unsymmetrical benzamidinate ligands (**32**) acts as single electron donors towards diphenyl dichalcogenides (Chart 5) [96].

The low reducing potential of Eu(II) can be overcome by photoexcitation. While Eu(II) is stable in neutral, protic solvents (e.g., water and alcohols), photoirradiation makes it reactive enough to reduce protons (Scheme 2) [97]. Irradiation of $EuCl_3$ at wavelengths slightly longer than 300 nm in alcoholic solutions yielded Eu(II). Further photoexcitation gave Eu(II)*, which was sufficiently reducing to transfer a single electron to 1,3-dimethyluracil (Scheme 3) [98,99]. The resulting radical underwent further reactions, providing regioselectively the hydroxymethylated uracil derivative. The same Eu(III)/Eu(II) photoredox system was also able to reduce different aliphatic and alicyclic alkenes [100].

Maity and Prasad investigated the charge separation state between different Eu(II) complexes and organic acceptors after UV light irradiation [101]. Benzyl bromides, alkyl bromides and iodides, benzaldehyde and acetophenone were tested. Detailed spectroscopic studies revealed that both forward and back electron transfer were feasible between Eu(II)* and the acceptors. In the case of carbonyl acceptors back electron transfer rates were found to be 4 orders of magnitude lower compared to the forward electron transfer, making the Eu(II) complexes suitable reductants for these substrates. Combining Ln metals with their divalent iodides enhanced the Ln(II) reactivity towards alkyl halides [102]. This was further increased by photoirradiation. It is unclear what the role of the Ln metal is, however, it could not reduce the alkyl halide in the absence of the LnI_2.

Reactivity can be attributed to Eu(II) formed *in situ* from Eu(III) upon photoexcitation in a small number of examples. Irradiation of an azido-Eu(III) complex with 333 nm light results in a LMCT state, which gives rise to Eu(II) and N_2 products [103]. Photoexcited Eu(III)(2.2.1) cryptand is reduced to Eu(II) with $[M(CN)_6]^{4-}$ (M = Os, Fe, Ru). The Eu(II)(2.2.1) in turn can reduce Ru^{3+} to Ru^{+} [104].

The photochemical reduction of Eu(III) to Eu(II) in the presence of sulfate ions, and the subsequent selective precipitation of the low-solubility $EuSO_4$ from the solution enabled the separation of Eu from mixtures with other rare earths (Y and Gd). This procedure provides a green alternative to existing Eu recovery methods from lamp phosphor wastes. The useful pH-range could be extended to higher values by conducting the reduction with ^{i}PrOH, which stabilized the reduced Eu(II) product, and thus increased the yield [105].

5. Conclusions

In luminescent complexes electron transfer from the excited antenna to Eu(III) is an energetically favored process that has been observed for a broad range of antenna structures. In the overwhelming majority of cases PeT is detrimental to Ln luminescence, and decreasing it improves Ln(III) emission appreciably. While driving force for PeT can be reduced by reducing the energy of the excited antenna, this also shifts the antenna excited singlet and triplet levels, which in turn may open up previously unavailable deactivation pathways (e.g., energy back transfer from the Ln to the antenna). An alternative method is the stabilization of the Eu(III) redox state by encapsulation into ligands with smaller cavity sizes and providing charge neutral complexes, or complexes with overall negative charges. The current shortcomings of this latter approach are twofold. First, there is a lack of systematic studies directed at stabilizing the Eu(III) redox state. Second, Ln complex structure influences in vivo behavior, which limits the extent to which ligands can be adjusted while retaining their utility in bioimaging.

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