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Metal complexes as components of luminescent signalling systems

A. Prasanna de Silva *, David B. Fox, Allen J.M. Huxley,
Nathan D. McClenaghan, Juliette Roiron

School of Chemistry, Queen's University, Belfast BT9 5AG, UK

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Contents

Abstract

Freshly developing lines of research in luminescent signalling with metal complexes over the last year are critically discussed. Metal-containing moieties are found to serve as remarkable lumophores with delayed emission and also as efficient receptors especially for anionic species. The photophysical concepts of metal-centred (MC) excited states, metal to ligand charge transfer (MLCT) excited states, metal–metal to ligand charge transfer (MMLCT) excited states, photoinduced electron transfer (PET) processes and electronic energy transfer (EET) processes are all being exploited during these signalling operations. Novel sensors and switches are emerging as a result. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Luminescent; Fluorescent; Sensors; Switches; Metal complexes

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* Corresponding author. Tel.: +44-1232-274422; fax: +44-1232-382117.
E-mail address: a.desilva@qub.ac.uk (A.P. de Silva)

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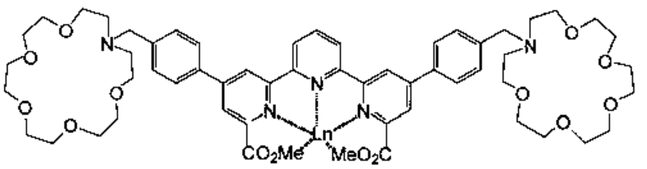
1. Introduction

Luminescent signalling is continuing to gain the attention of laboratories worldwide as a powerful route to molecular sensors and switches. The recent appearance of two comprehensive reviews [1,2] and a multiauthored volume [3] will facilitate access to the previous literature in the area. Our aim in this report is to focus on some of the latest developments which exploit the special features of metal centres. Parallel achievements concerning metal-free luminescent signalling will therefore fall outside the scope of this article.

2. Metal complexes as lumophores

Lanthanide complexes have a history of over half a century as unique lumophores [4]. From an experimental viewpoint, their uniqueness is their line-like emission in the frequency domain and their delayed emission in the time domain. These features, especially the latter, permit more sensitive signal detection in real-life matrices than is possible with other types of emission. In spite of this obvious advantage, there were only a handful of signalling systems based on lanthanide complexes prior to 1997. The pace has been quickening since then.



1

Our K^+-responsive system **1** shows a smooth luminescence enhancement upon arrival of the alkali cation if the lanthanide core is chosen to be Eu(III) [5]. The terpyridyl diester moiety serves as the antenna which efficiently gathers the incoming photon. In the present context, an antenna is taken to be a unit which readily absorbs light and transfers the energy efficiently to a second moiety which is a poor intrinsic absorber. Multiple absorbing units are not necessary. However, we must remain aware of other contexts where the antenna effect is enhanced by the use of chromophore arrays. For instance, dendrimers with aromatic branches are the newest addition to the range of available antennas [6]. Population of the metal-centred (MC) excited state occurs by electronic energy transfer (EET) from the antenna. This $^5D_0$ state is intrinsically emissive especially because the metal centre is substantially, though not completely, protected from high frequency oscillators such as hydroxyl groups in any coordinated solvent molecules. However, emission is thwarted by an additional deexcitation pathway designed into the system. In other words, the luminescence is switched 'off' in the absence of K^+. This is achieved by connecting the monoaza-18-crown-6 ether units via methylene spacers to the antenna. The azacrown nitrogen lone electron pairs participate in a photoinduced electron transfer (PET) process with the antenna and/or Eu(III) centre. In contrast, K^+ capture by the azacrown units raises the barrier to electron removal from the nitrogen lone pairs. Thus the PET process loses out in the competition with luminescence emission from the MC state or the process producing the MC state.

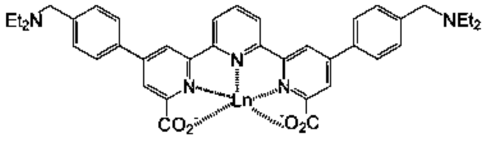
The clear K^+-responsive behaviour of **1** virtually disappears if the lanthanide centre is Tb(III) instead of Eu(III). The Tb(III) complex has its MC excited state only 4.1 kcal mol^{-1} below the triplet state of the antenna. Hence thermally assisted back EET prevails over emission as the prime route depopulating the MC excited state. It is remarkable that **1**'s close cousin **2** showed robust luminescent sensor behaviour when Tb(III) is the featured lanthanide [7].

The key to this behavioural divergence is that the antenna triplet energy of **2** is significantly higher than in the case of **1**. Phosphorescence studies at 77 K performed on the Gd(III) complexes of **1** and **2** clearly show this divergence. Using the Gd(III) complexes ensures that the conformation of the ligands are essentially identical to their Tb(III) and Eu(III) counterparts. Evidently, the carboxymethyl ester groups in **1** and the carboxylate groups in **2** contribute differently to the electron delocalisation in the two triplet excited states.

In the hands of David Parker and his colleagues, the combination of 12-ane-N_4 complexed lanthanide(III) lumophores and heteroaromatic antennas have yielded several different sensor systems.

The Eu(III) case **3** with an amidomethylphenanthridine antenna shows a significant bathochromism upon protonation. Judicious long wavelength irradiation will therefore only cause excitation of the protonated sensor. Intense emission arises only under these conditions and a huge luminescence enhancement factor of > 500 is the result [8]. On the contrary, the Tb(III) counterpart shows its characteristic green emission only when the sensor is unprotonated provided that irradiation is suitably short-wave to cause excitation [9]. The relatively high energy of the Tb(III) $^5D_4$ state means that the antenna triplet state lies high enough above the MC excited state only when unprotonated – a consequence of the proton-induced bathochromism mentioned above. Even then, the antenna triplet is close enough to the MC excited state to permit back energy transfer. Dioxygen is thus able to quench the antenna triplet whose intrinsic lifetime has been extended by the above process. The pH sensory Eu(III) case **3** can be converted to sense halide by simple quaternisation of the phenanthridine nitrogen. Otto Wolfbeis provided a foundation by noting that the fluorescence of quinolinium ions is quenched by halides, presumably via a collisional charge transfer mechanism [10]. Thus the energy is drained from the antenna excited state by halide ions before it is transferred to the Eu(III) centre. Halide-induced quenching of the Eu(III) emission is the outcome [8]. Phenanthridinium ions will react in a more drastic fashion with more nucleophilic agents such as OH^-, destroying the antenna π-system in the process. So this Eu(III) case also shows strong emission quenching in the strongly alkaline regime [8].

Multiplication of antennas in these cases also multiplies receptors. The emission-pH profiles of multireceptor sensors are known to produce multiple steps which in favourable cases can merge to produce extended dynamic ranges [11,12]. We note that each receptor is expected to participate in mass action-type equilibria which cause the receptor population to move from being 90% proton-free to 90% proton-bound over a range of 2 pH units. So the tetra-antenna Eu(III) case **4a** naturally shows overlapping emission-pH steps 3–6 and 6–8 with different slopes [13].



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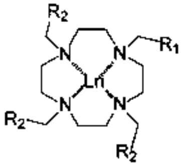
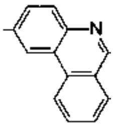
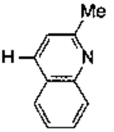


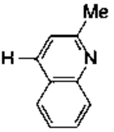
3 ; R_2 = P(=O)(Me)O$^-$; R_1 = CONHCH$_2$–



4a ; R_1 = R_2 = CONH–

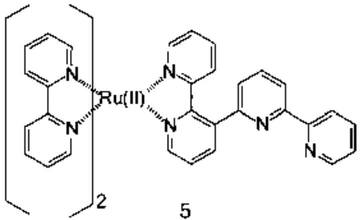


4b ; R_2 = P(=O)(Me)O$^-$; R_1 = CONH–



Surprisingly, a rather parallel function with two steps with different slopes can also be discerned in the case of the Eu(III) containing mono-antenna version **4b** except that it is displaced about 1 pH unit in the alkaline direction because of the neutral rather than cationic nature of the complex. The smaller step may arise from protonation–deprotonation equilibrium involving a single water molecule bound to Eu(III). Such water molecules are known to be emission quenchers, but how that would affect the present case is unclear. System **4a** has the additional utility of being pH-sensitive across the 9–11 range if the fluorescence emission from the antennas is observed.

Ruthenium(II)-based systems also continue to produce very interesting luminescent switching actions. Their emission lifetimes in the μs range can be considered to qualify them as delayed emitters, the property that is bringing lanthanide lumophores to the fore of signalling research. We focus on some of the combined efforts of Francesco Barigelletti, Michael Ward and their teams.



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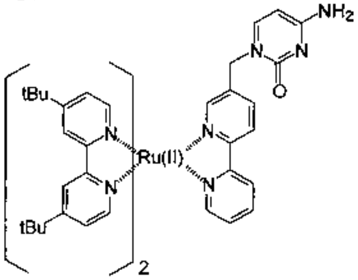
Complex **5** consists of the classical tris(2,2′-bipyridine)$_3$Ru(II) lumophore with another 2,2′-bipyridine unit directly appended so that it is sterically deconjugated from the rest of the structure [14]. The lone 2,2′-bipyridine moiety plays the role of a proton receptor in two distinct stages. Complex **5** is strongly luminescent prior to protonation. The first protonation results in a red-shifted, but still strong, emission owing to the proton-induced stabilisation of the metal to ligand charge transfer (MLCT) excited state. The second protonation has much more drastic consequences: the luminescence is entirely switched 'off'. A PET process is the likely culprit since the system is a virtually spaced lumophore–receptor pair [15] and because diprotonated bipyridines are reminiscent of the powerful electron acceptor methylviologen. Case **5** therefore nicely complements two other PET sensors based on the tris(2,2′-bipyridine)$_3$Ru(II) lumophore due to Ron Grigg and colleagues which employ aromatic amine [16] and phenolate [17] receptors to produce the pH-switchable luminescence.

The mutual recognition of guanine–cytosine and adenine–thymine pairs can also be brought into the framework of metal complexes for the purposes of luminescence signalling. Tris(2,2′-bipyridine)$_3$Ru(II) complex with an appended cytosine **6** and the corresponding Os(II) complex with an attached guanine **7** [18] come together in CH_2Cl_2 solution to set the stage for an EET process between the classical energy transfer couple of Tris(2,2′-bipyridine)$_3$Ru(II)/Os(II).



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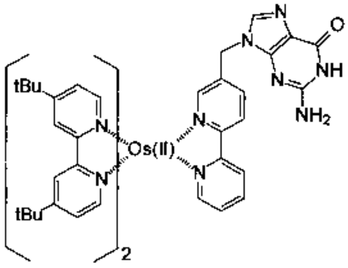

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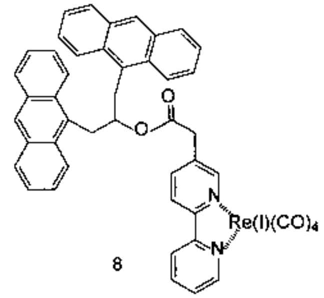
EET mediated by the triple hydrogen bond array is clearly seen by both steady state and time resolved luminescence studies. This work joins a small band of hydrogen bond-mediated EET systems, none of which involves metal complexes [19–21]. Unfortunately only the luminescence emanating from the Ru(II) moiety could be observed in the present case. The corresponding adenine-appended Ru(II) complex and the thymine-appended Os(II) complex associate far more weakly than **6** and **7** [22]. Luminescence signalling experiments are therefore thwarted for the time being.

Some of the newest luminescent switch systems are not triggered by chemical species, but rather by light of a wavelength different to those involved in the luminescence processes.



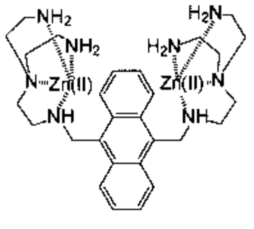
8

Complex **8** is hardly emissive due to EET to the anthracene units [23]. On the other hand, the bisanthryl bipyridine ligand can be converted to the anthracene photodimer by $4\pi + 4\pi$ cyclisation. This is accomplished by 256 nm irradiation. Now the bipyridine ligand is devoid of the extended π-system with a low lying triplet state. The tetracarbonyl Re(I) complex of this bipyridine ligand containing the anthracene photodimer is therefore brightly emissive. The photocyclised ligand can also be smoothly photocycloreverted by 388 nm irradiation. However, such smooth switching between the two forms is harder to achieve in the case of the preformed Re(I) complexes presumably due to sapping of singlet energy in the anthracene or anthracene photodimer components by the sink at the bipyridine Re(I) unit.

3. Metal complexes as receptors

It has been clear for some time that metal centres can provide ways of binding electron rich species. The newest research along this direction appears to concentrate on marrying fluorescence switching schemes to receptor arrays with sharpened selectivities. As an illustration, a pair of tetra-amino Zn(II) complexes held apart by a 9,10-anthryldimethyl backbone proves to be an excellent motif for the selective fluorescent sensing of ambidentate anions, as demonstrated by Luigi Fabbrizzi's laboratory [24,25]. The receptor nature of each Zn(II) centre is clear since each possesses a vacant coordination site. Zn(II) is benign as far as emissive photophysics is concerned, since its lack of d-d excited states or redox states prevents EET or PET processes. The 9,10-anthryldimethyl backbone has seen similar service in metal-free sensing contexts [26–28] as has the 2,8-isomeric component [29].

The dizinc(II) complex **9** efficiently captures imidazole derivatives such as histidine with the exclusion of all other amino acids around pH 10 [24]. Deprotonation of the imidazole unit accompanies capture. Now a PET process becomes feasible between the imidazolate and the anthracene fluorophore. Hence histidine binding is signalled by switching 'off' fluorescence, though the switching factor is limited to a factor of 2. However, the parent imidazole produces a larger switching factor of 5.



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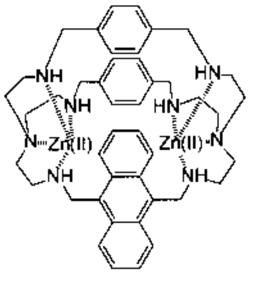
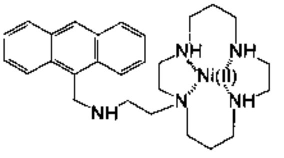


10

Structural elaboration of **9** into the cryptate **10** is a natural way of increasing the anion selectivity of the receptor [25]. Only small linear ambidentate ligands like NCO^- and N_3^- enter the cavity. Larger and smaller anions such as NO_3^- and Cl^- respectively are successfully rejected. Anion binding is again transduced into a switching 'off' of the fluorescence signal, though this time by an order-of-magnitude in the case of the redox active N_3^-. A further photophysical sharpening of selectivity occurs here since NCO^- does not trigger a PET process in **10** and hence the fluorescence is unaffected.

Such research can have applications beyond the sensor area. For instance, square planar Ni(II) can take on additional axial ligands, which is seen with Luigi Fabbrizzi's **11** as the pH is increased [30]. As soon as it is neutral, the exocyclic amine swings over the Ni(II) centre. The remaining axial position is taken up by a water molecule. Since the anthracene fluorophore is now closer to the Ni(II), its fluorescence is moderately quenched by EET from the anthracene singlet excited state to the MC d-d state. Further increase of the pH deprotonates the axial water which triggers PET from the Ni(II) centre to the anthracene moiety to kill the fluorescence. Switching of a fluorescence signal between 'high', 'low' and 'off' constitutes a molecular tristable system-a situation also seen by Ron Grigg and Amila Norbert a few years ago [31]. The fact that this is coupled to an intramolecular movement in one of the stages is of additional interest in the context of molecular machinery [32].



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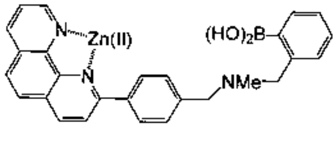
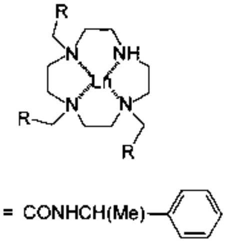


12

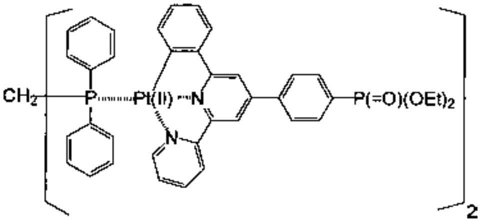
4. Metal complexes in dual roles

In contrast to the cases discussed in the previous section, the use of aromatic ligands in the construction of coordinatively unsaturated metal complexes opens the way to receiving guests while simultaneously being emissive. This is nicely illustrated by the selective signalling of monosaccharide acids with Seiji Shinkai's **12** [33,34]. The phenanthrolineZn(II) unit serves as the lumophore (though not of high efficiency) and as the receptor for the carboxylate moiety of say, D-glucuronic acid. A diol motif of the monosaccharide acid is bound by the 2-aminomethylbenzeneboronic acid component. The remarkable efficiency of the latter at binding monosaccharide derivatives and subsequently losing its PET donor ability towards suitable fluorophores has been established by the Shinkai laboratory. So it is no wonder that **12** shows substantial fluorescence enhancements with D-glucuronic acid whereas no such host–guest interaction can even be detected if the metal centre is removed.

Aromatic ligands are not essential for metal complexes to serve in dual roles of receptor and lumophore if the metal is intrinsically emissive. This, of course is the case with lanthanide complexes. Nevertheless, the importance of the antenna effect dictates the presence of aromatic units within the supermolecule. This scenario is found in David Parker's tricationic **13** [35]. The tricarboxamido 12-ane-N_4 ligand leaves room for two coordinated waters to the lanthanide centre. Good evidence for this hydration number comes from the influence of heavy water on the emission lifetime. The energy sapping effect of high frequency O–H oscillators can be curbed even more efficiently by displacing the water molecules with divalent anions such as bicarbonate. This produces significant luminescence enhancements with HCO_3^- in the case of the Eu(III) complex even under simulated clinical conditions.



13; R = CONHCH(Me)—



14

There is even more of a history of metal complexes receiving environmental information which is then relayed as a luminescence signal. A new example with an interesting twist is **14** due to Chi-Ming Che and associates [36]. Environmental modulation of metal–metal interactions is obviously achievable only with certain dinuclear complexes with a degree of flexibility. This can show up in luminescence from metal–metal to ligand charge transfer (MMLCT) excited states. Such emission from **14** can be observed if hydroxylic solvents with coordination capacity are avoided. However it is possible to hide **14** in non-coordinating microenvironments even within water if detergent micelles are employed. The degree of water penetration into micelles can be minimised by reducing head-group repulsions with high concentrations of NaCl. Under these conditions, MMLCT emission is indeed seen. Interestingly, NaCl-free micelle solutions of **14** show only MLCT emission diagnostic of mononuclear excited states.

Acknowledgements

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