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Combining luminescence, coordination and electron transfer for signalling purposes

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Contents

Abstract

The evolution of research in luminescent signalling at Queen's University of Belfast is critically reviewed in the context of related work from the literature. Photoinduced electron transfer (PET) is found to be a robust design principle for such work. The possibilities raised by these signalling systems for sensing and switching operations are pointed out. Fluorescent PET signalling systems for s-block metal ions and relatives are classified according to the type of receptor employed. PET signalling systems, which exploit lanthanide lumophores are also woven into the discussion.

Keywords: Luminescent; Fluorescent; Signalling; Crown ethers; Cryptands; Amino acids; Polypyridyls

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1. Introduction

The all-pervasive nature of chemical species means that their observation is of critical importance if we are to understand what is around and within us. Since atoms and molecules operate on a space-scale which is far smaller than ours, we need specially equipped molecules positioned at the scene to report on the action [1]. Among their special capabilities, our reporter molecules must have a means of bridging the nanometric and metric space-scales. Photonic transactions can easily provide this facility. Light absorption and emission [2] are equally comprehensible to molecules and people.

What is needed next is a means of encoding information from the molecular world within the light signal. While this can be achieved in several ways, we focus on light intensity in the present instance. At the extreme this can be the qualitatively distinguishable 'on' and 'off' states. Quantitation is easily achieved by measuring the intermediate situations. These arise naturally if a population of reporter molecules are arranged to partition between 'on' and 'off' states. Since such partitioning of populations are commonly seen in mass action-type equilibria [3], we aim for the latter with regard to molecular interactions between the reporter and its target. Reporter-target interactions, especially those involving ion coordination [4], can be of sufficient strength to cause the required 'off' and 'on' states of light intensity if appropriate photochemical processes are brought into play. After all, the susceptibility of molecular luminescence towards quenching is well-advertised in textbooks on the subject [2,5]. Electronically excited states of molecules are sufficiently long-lived by nature (of the order of nanoseconds) to suffer deactivation by encounters with external but not necessarily extramolecular entities. Intrinsically quenching target species will obviously switch a luminescent reporter from 'on' to 'off' [6]. 'Intrinsically quenching' would be a catch-all phrase covering a range of de-excitation mechanisms. However there are many important targets which are not blessed with that capacity. So it becomes imperative to build in the quencher close to the luminescent heart of the reporter. Then we only need to arrange for suppression of the quenching mechanism upon capture of the target. Luminescent 'off–on' signalling of a whole gamut of targets now comes into view [6].

However once built into the reporter, most of the known quenching mechanisms have usually not been 'smart' enough to be responsive to the arrival of the target species, according to the evidence in the literature so far. Pathways involving alkene units, weak bonds, paramagnetism, heavy atom effects and electronic energy transfer (EET) fall into this category, though there are serious ongoing efforts to perturb the latter by placing the target in the path of EET [7]. Also a clever approach is available in specific cases to suppress fluorescence quenching pathways in alkene units [8]. The quenching mechanism based on low-lying $n\pi^*$ excited states provides a welcome exception by responding rather sharply to target species which engage the lone electron pairs responsible for the $n \rightarrow \pi^*$ transition [9]. Good examples from the recent literature can be found in the work of Prodi and Sykes and their colleagues [10,11]. However, the 'smart' mechanism, which has yielded the greatest harvest so far is photoinduced electron transfer (PET) [12,13]. This will

exclusively occupy our attention throughout the rest of this paper. As we have comprehensively reviewed this general area recently [6a,14], the present focus will be on the evolution of our contributions. These will be classified according to the type of receptor within each signalling system.

2. Design principle

The principle of luminescent PET sensing is summarized in Fig. 1 [1]. We note the three-module 'Lumophore–Spacer–Receptor' format [15] which permits electron transfer from the receptor to the lumophore (or vice versa) if the process is thermodynamically and kinetically feasible [16]. In most instances so far, kinetic restrictions are minor though exceptions are coming to light [17,18]. Importantly, the electron transfer rate in many favourable cases is much faster than the luminescence rate when PET is thermodynamically allowed. Luminescence and electron transfer are the two main competitors, which deactivate the photoexcited state of these designed systems. Binding of the target species (typically a metal ion) to the receptor can drastically alter PET thermodynamics to an endergonic situation. At the simplest level, this situation is caused by electrostatic interactions between the receptor–target pair. Luminescence is now the winner of the competition. Luminescence can thus be switched between 'on' and 'off' states by introduction and removal, respectively of the target species, which provides us with the responsive quenching mechanism we needed.

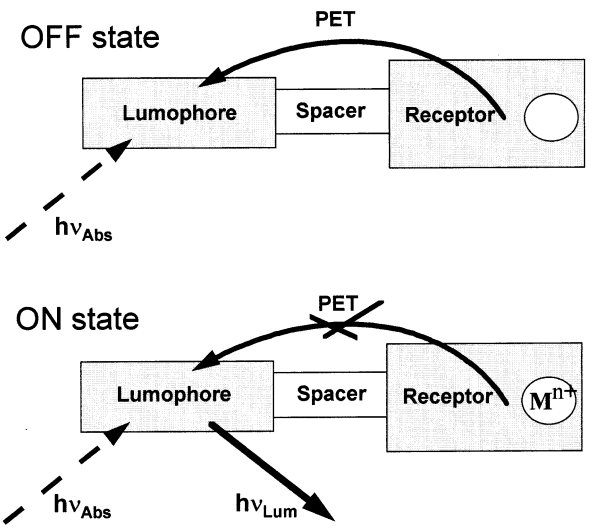
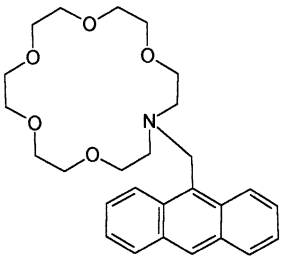


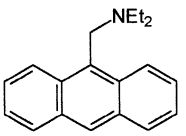
Fig. 1. (a) The thermodynamic condition for PET is that the excited state energy of the lumophore must be larger than that required to oxidize the receptor and to reduce the lumophore. (b) By introducing a target, i.e. metal ion, into the receptor cavity its oxidation potential is raised, causing the thermodynamic condition for PET to be removed.

3. Azacrown ethers

Our first effort in this photophysical aspect of coordination chemistry concerned **1** [19]. This was a rational outgrowth from the proton signalling system **2** [15,20].

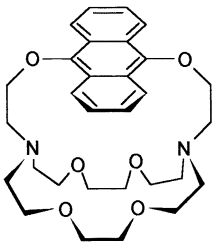


1



2

The simple amine group within **2** was elaborated into an azacrown ether within **1** for the purpose of signalling alkali cations. The presence of the basic nitrogen obviously required the use of a proton scavenger such as benzyltrimethylammonium hydroxide so that the influence of metal ions upon **1** could be unequivocally demonstrated. K^+ induced excellent 'off–on' fluorescence signalling with a fluorescence enhancement (FE) factor of 47 in methanol as solvent. Deeper investigation revealed that the binding constant between **1** and a given alkali cation was virtually identical to the corresponding value exhibited by the parent azacrown ether. At the simplest level, this confirmed the modular behaviour of the system **1** in the sense of Fig. 1 since the coordination parameters of the receptor component were quantitatively preserved. The photophysical parameters, i.e. wavelengths of absorption and emission, extinction coefficients of the 9-methylanthracene fluorophore were conserved as well. Quantum yields of fluorescence of **1** induced by alkali cations approached, but fell short of, the corresponding value of the fluorophore module. A related pioneering example **3** from Bordeaux and Strasbourg used anthracene and diazacrown ether units juxtaposed within a cryptand structure [21]. System **3** displayed smaller FE factors; perhaps because its elaborate structure hindered optimal solvation of radical ion pair intermediates which in turn slowed PET in the metal-free state. Since then the special coordination capability of crown ethers and the emission properties of aromatic hydrocarbons have been combined by Kubo et al. with varying degrees of success [22]. An *N*-phenylazacrown ether receptor within **4** [23] offered some protection against protonation and gave excellent fluorescence enhancement with Ca^{2+} in acetonitrile. Besides the FE factor of 28, an increase of fluorescence lifetime from 0.28 to 3.6 ns was found.



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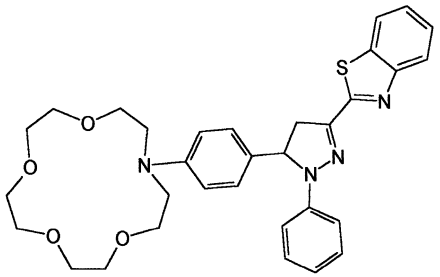
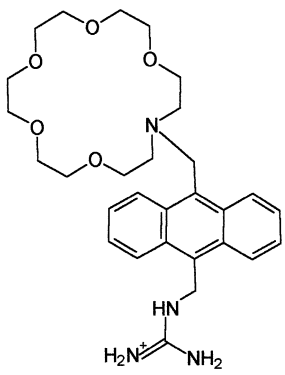


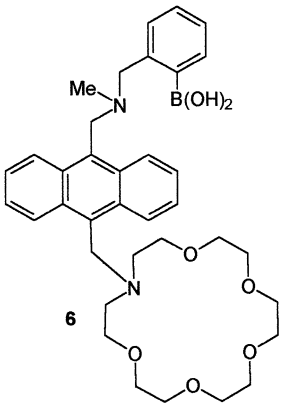
4

As azacrown ethers can also bind ammonium cations, **1** was further developed into **5** to recognise γ-aminobutyric acid (GABA) zwitterions with some selectivity [24]. The carboxylate terminal of GABA was held by the guanidinium moiety of **5**. Anslyn has recently exploited guanidinium–carboxylate interactions to sense citrate fluorimetrically [25]. The anthracene fluorophore within **5** also contributed critically to the selectivity of target recognition by restricting the azacrown ether and the guanidinium units to a relatively narrow band of separation distances. While the anthryl-9,10-dimethyl spine is not ideal for recognising GABA from a series of α,ω-ammoniumalkanecarboxylates, the synthetic accessibility of **5** more than compensates for this shortfall. Additionally, the proton sensitivity that comes with the use of **1** as a building block had to be controlled by working with **5** at pH 9. Nevertheless the significant fluorescence enhancement produced by **5** in the presence of GABA opened up a worthwhile approach to tracking this critical neurotransmitter.



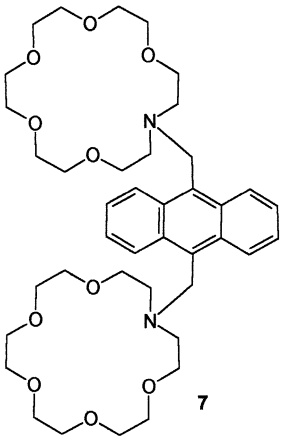
5

Cooper and James also used **1** as the starting point for their excellent fluorescent sensor **6** for glucosamine [26]. Again, careful pH control was required but near-neutral conditions were found to be satisfactory. System **6** also used the aminomethylphenylboronic acid unit with a proven track record for saccharide binding. The 'off–on' signalling occurred with glucosamine but not with glucose since two PET active receptors were present within **6**, one binding ammonium and the other accosting a diol motif.



6

Two PET active receptors were also present within **7** [27], which was another outgrowth from **1**. The anthryl-9,10-dimethyl spine again brought a degree of length recognition. α,ω-alkanediammonium ions were the targets and excellent fluorescence enhancements were found. As perhaps expected, monoammonium ions give similar responses only at much higher concentrations. Interestingly, **7** responded best to putrescine and cadaverine dications which are naturally produced within decaying biomaterial. The anthryl-9,10-dimethyl spine has also featured in Fabbrizzi's design for the fluorescent sensing of imidazole derivatives [28] while the anthryl-1,8-dimethyl spine has been exploited by Vance and Czarnik for sensing pyrophosphate [29].

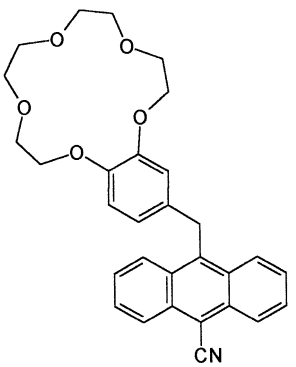


7

4. Benzocrown ethers

The inherent Brønsted basicity of azacrown ethers requires careful pH control in any signalling systems containing these components. In less favourable situations, the fluorescence response towards a chosen target, could be swamped by protonation effects in spite of the best efforts. Additionally, some important phenomena cannot be unequivocally demonstrated if the possibility of protonation is present. So we have looked to benzocrown ethers as relatively proton-insensitive receptors for alkali cations. Receptors must be suitably electroactive for incorporation into PET signalling schemes. The presence of the 1,2-dialkoxybenzene unit confers the required electroactivity, even though its oxidation potential is somewhat higher than that for a tertiary aliphatic amine centre in an azacrown ether.

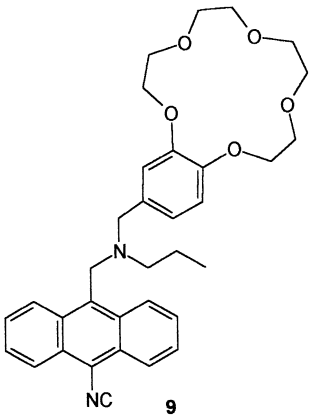
When this allowance is made, we obtain fluorescent signalling systems for alkali cations with virtually no interference from protons. System **8** [30] responded sensitively to Na^+ and was an early testimony to the general success of the PET sensor design principle. This is because the receptor–target interaction is far from ideal, given that only a fraction of the electroactive group is directly bound to the ion and that axial solvation reduces the electrostatic effect of the ion. As a bonus, the difference in PET thermodynamics between the ion-free and ion-bound states of **8** can be optimised by solvent variation to produce increased fluorescence enhancements with Na^+ [31].



8

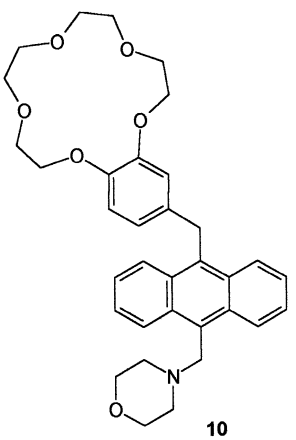
The combination of a benzocrown ether receptor for Na^+ and a simple amine receptor for H^+ within a fluorescent PET system allowed us to produce more complex 'off–on' signalling operations. The essential specificity of each receptor towards its corresponding target was a critical consideration. System **9** clearly contains motifs seen within simpler molecules **2** and **8** [32]. It is remarkable that ion-controlled photophysics [33] of multimodular systems [34] can lead us to switching phenomena more reminiscent of information technology [35]. 'Fluo-

rophore–Spacer$_1$–Receptor$_1$–Spacer$_2$–Receptor$_2$' system **9** represents a two-input AND logic operation at the molecular scale provided we view H^+ and Na^+ as the two inputs, fluorescence as the output and exciting light as the power supply. From a mechanistic viewpoint, both PET processes arising from the benzocrown ether and the amine receptor must be eliminated by complexation of Na^+ and H^+, respectively before a relatively high level of fluorescence is seen.



9

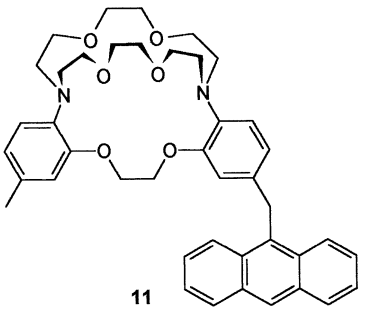
AND logic gate **9** required optimisation because the quantum yield of fluorescence in the 'on' state was low as were the FE factors. This was accomplished by minimizing the separation distance of both receptors from the fluorophore to produce system **10** [36]. This produced fast PET from each receptor when it was ion-free so that very low fluorescence quantum yields were achieved in the 'off' state. Once both receptors were ion-bound, the 9,10-disubstituted anthracene fluorophore was almost ideally emissive. Excellent FE factors were the result. Nice examples of related logic systems are now available from the laboratories of Iwata and Tanaka [37], Pina, Balzani and their colleagues [38–40], Parker and Williams [41]. System **6** [26] also fits into this small group.



10

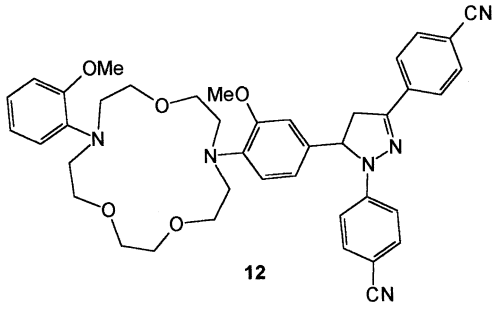
5. Cryptands and relatives

The extension of azacrown ethers into the third dimension gave cryptands with enhanced receptor capability [4]. Cryptands would also attenuate the axial solvation of the target ion seen with the two-dimensional benzocrown ethers. The basicity of the bridging nitrogen atoms needs to be lowered; however, due to the protonation problem indicated in Sections 3 and 4. Conjugation of aromatic units to the offending nitrogens provided an adequate solution to this problem as mentioned regarding **4**. A bonus was that such conjugation could be decoupled by a conformational change that accompanied binding of the target ion. Thus the oxidation potential of the receptor is expected to increase over and above that anticipated from electrostatic consideration alone. Since the PET thermodynamics with suitable fluorophores can now enter the endergonic regime more easily, reasonably high FE factors resulted in the case **11** with Rb^+ and K^+ [42].



11

There are advantages to be gained by employing pseudocryptands as receptors within PET signalling systems. Besides somewhat shorter syntheses, the greater flexibility of pseudocryptands allowed the ion-induced conformational change to achieve more of its potential. Good switching 'on' of fluorescence was seen with **12** and Na^+ [43]. Even Li^+ produced a similar response though at higher concentrations. Again, the aniline-type nitrogens caused no difficulties with protonation at neutral pH. The receptor within **12** was dissected from Tsien's excellent Na^+ sensor [44], which functioned with a mechanism quite distinct from PET [45]. Clear evidence for the ion-induced conformational change was obtained from X-ray crystallographic structure determination of the receptor unit of **12** before and after Na^+ binding. Aryl–nitrogen conjugation was eliminated upon Na^+ complexation with a rotation of 39° about the aryl carbon–nitrogen bond [43].

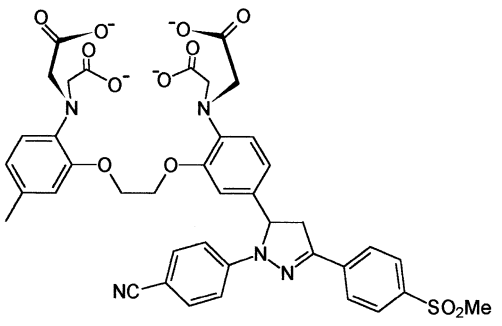


12

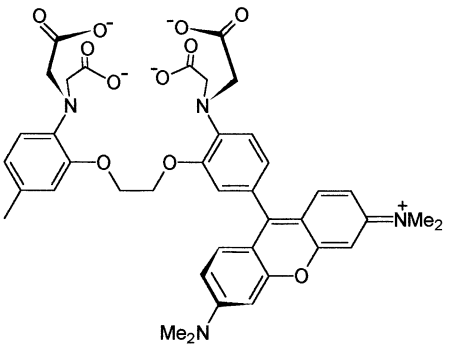
The conformational change discussed above, contributed to the observation of rather similar FE values with target ions of differing charge density in both **11** and **12**. This contrasted with the behaviour of structurally similar systems, e.g. **1**. At first sight, this aspect of **11** and **12**'s signalling capability might be considered a disadvantage since it suggests a total loss of selectivity. This suggestion is rather illusory because luminescent signalling systems possess two selectivity parameters — quantum yield enhancement and ion binding constant. Maintaining selectivity in one parameter and achieving nearly ideal non-selectivity in the other can lead to interesting possibilities such as molecule-based OR logic gates [32,46,47] with ion input and photon output.

6. Amino acids

While undoubtedly useful, macrocyclic receptors are not essential for the proper operation of luminescent PET signalling systems. In fact, the extra flexibility of acyclic receptors can allow the ion-induced conformational change to operate at full strength. System **13** allowed us to demonstrate this point [48] with regard to Ca^{2+} signalling under simulated physiological conditions. Interchangeability of the fluorophore unit between heterocycles and hydrocarbons while preserving the Ca^{2+} response demonstrated the broad foundation of the PET signalling design. The 'off–on' signalling capability and almost all the signalling parameters (optical and coordination) of **13** were quantitatively predictable from data available for the fluorophore and receptor modules. As in the case of **12**, the receptor unit within **13** came from previous work by Tsien. His Ca^{2+} receptor displayed excellent selectivity against most other cell constituents [49]. Several popular fluorescent sensors have arisen from this elegant research programme [49–52], some of which have received PET rationalizations [52,53]. System **14** was studied by both Minta et al. [54] and ourselves [55]. We were able to demonstrate that **14** fitted the criteria for a 'Fluorophore–Receptor' system where the two components are orthogonal, i.e. virtually spaced, thus allowing rapid PET to occur in the Ca^{2+}-free state.

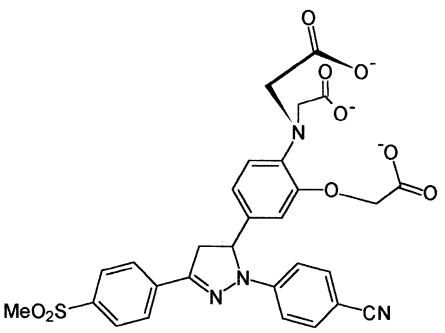


13



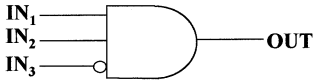
14

London's Mg^{2+} receptor [56] was the inspiration behind **15** [46] which also showed essentially 'off–on' fluorescence signalling with physiological levels of Mg^{2+}. Remarkably Ca^{2+} also produced virtually the same FE value, though the concentrations required are much higher than those associated with most cell types. So **15** can serve as a selective sensor for Mg^{2+} in physiological regimes while also functioning as a nearly ideal photoionic OR logic gate (discussed in Section 5).



15

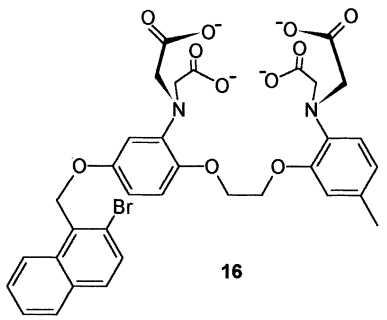
A Tsien Ca^{2+} receptor [50] was again at the heart of our recent effort to increase the viability of molecular-scale information processing with luminescent PET signalling systems. AND or OR logic gates described in Sections 4–6 require a minimum of two inputs. Simpler logic gates, i.e. NOT only need one input. Creation of higher-level logic systems requires integration of lower-level devices. For instance the INHIBIT gate, as usually represented, requires three inputs at a minimum and requires a particular combination of AND and NOT logic. Its electronic symbol and truth table are shown in Fig. 2. Integration comes naturally to present day silicon systems because the inputs and outputs are all electronic. Integration is a much harder challenge for molecular-scale logic operations with the particular approach outlined earlier. On the other hand, all-electronic molecular-scale logic devices are yet to be demonstrated. The challenge of integration has been



IN_1	IN_2	IN_3	OUT
0	0	0	0
0	1	0	0
1	0	0	0
1	1	0	1
0	0	1	0
0	1	1	0
1	0	1	0
1	1	1	0

Fig. 2. Electronic symbol and truth table for the INHIBIT logic gate.

taken up in INHIBIT gate **16** [57]. In the language of Fig. 2, $IN_1 = Ca^{2+}$, $IN_2 = \beta$-cyclodextrin, $IN_3 = O_2$, OUT = phosphorescence intensity. Ca^{2+} binding to the amino acid moieties within Tsien's receptor stops PET involving the bromonaphthyl phosphor. Phosphorescence is also susceptible to PET-caused switching [58]. However, phosphorescence emission cannot be observed without enveloping the phosphor with a transparent shield such as β-cyclodextrin. This prevents triplet excited states centred on bromonaphthyl phosphors from encountering and deactivating each other. Intense phosphorescence emission still requires the absence of O_2. As a small paramagnetic molecule, O_2 wreaks havoc on magnetic triplet excited states. In the present case of **16**, O_2 deactivates the triplet excited state in spite of the reversible protection offered by the β-cyclodextrin shield. So O_2 serves as the special disabling input (IN_3) for the INHIBIT gate. v

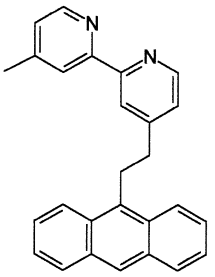


16

7. Polypyridyls

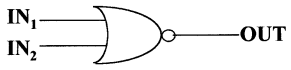
Polypyridyl units have greatly enriched supramolecular photochemistry [12,59] when they are essentially irreversibly combined with Ru(II) and Os(II) centres to

give the corresponding luminescent complexes. Our efforts have gone into the use of polypyridyls as kinetically reversible receptors. For instance the previously known compound **17** [60] can now be shown to act as a NOR logic gate [57] which integrates NOT and OR functions (Fig. 3). As with **16**, the integration is achieved functionally without attempting the difficult task of physically linking molecular logic gates and other components. The bipyridyl receptor binds either H^+ or Zn^{2+}. Flattening and electrical charging of the receptor leads to rapid PET from the excited state of the anthracene fluorophore. Hence the fluorescence output from **17** is only observed if IN_1 (H^+) and IN_2 (Zn^{2+}) are both absent.



17

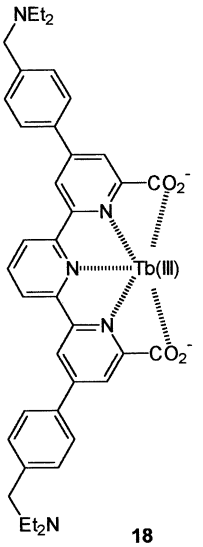
Receptors can capture not only target analyte species but also luminescent f-block metal ions. Thus efficiently luminescent assemblies can be constructed from aromatic receptors which avidly absorb light and transfer this energy to the metal centre for subsequent emission. Another aspect of efficiency arising from the receptor is its protection of the metal centre from energy-draining high-frequency oscillators such as coordinated waters. These lanthanide lumophores are distinguished from conventional fluorophores by their extended lifetimes of emission in the ms regime. Time-resolved observation following flash excitation thus permits interference-free monitoring even in highly fluorescent environments [61]. Signalling research can benefit from this remarkable feature if we build 'Lumophore–$Receptor_1$–Spacer–$Receptor_2$' systems. We note that the $receptor_1$ component complexes a lanthanide lumophore whereas the $Receptor_2$ unit binds a target analyte species as usual. The arguments regarding PET thermodynamics outlined in Section 2 remain in force.



IN_1	IN_2	OUT
0	0	1
0	1	0
1	0	0
1	1	0

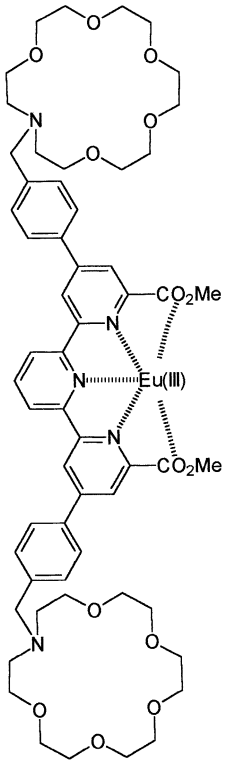
Fig. 3. Electronic symbol and truth table for the NOR logic gate.

A terpyridyl dicarboxylate receptor held the Tb(III) lumophore [62] within **18** while a pair of simple amine receptors provided H^+ binding capacity [63]. Good switching 'on' of luminescence occurred in acidic solution. The success of **18** could be attributed at least in part to the triplet state lifetime of the terpyridyl dicarboxylate which was extended by back energy transfer from the Tb(III) centre. The triplet state lay only 1750 cm^{-1} above the $^5D_4$ excited state of Tb(III), thus permitting population of the upper state at room temperature in the Boltzmann sense [64]. PET involving triplet states was previously discussed with regard to **16**.



18

While **19** with its azacrown ether receptors could have quite legitimately belonged in Section 3, its most remarkable feature arose from the dicarbomethoxy terpyridyl receptor–Eu(III) assembly. Hence its inclusion here. System **19** was the first example of a metal-centred luminescence being switched 'on' by a second metal ion [65]. The second metal ion K^+ fitted neatly into the aza-18-crown-6 ether cavity. So **19** became a higher generation version of **1** with the accompanying advantages of delayed luminescence. Interesting output from Rudzinski et al. [66] and Parker et al. [67,68] contribute to the momentum of this research line.



19

8. Conclusion

We hope that the above discussion will encourage more laboratories to exploit coordination chemistry as a sensitive means of biasing the competition between photoinduced electron transfer and luminescence. The design of powerful luminescent sensors and switches will then be accelerated. The former will be useful solutions in monitoring problems in a variety of contexts. The latter should create interesting possibilities for molecular information handling.

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