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Luminescent molecular sensors based on analyte coordination to transition-metal complexes

Cerrie W. Rogers, Michael O. Wolf*

Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

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Contents

Abstract

Recent research towards luminescent molecular chemosensors in which sensing is achieved via binding of analytes as ligands to metal-based receptors is described. In some cases, the metal complex acts both as receptor and lumophore; in others, a pendant lumophore is coordinated to the metal receptor. Analyte binding can occur at a vacant coordination site on the metal chemosensor, or alternatively by displacement of a weakly bound ligand. In the latter case, hemilabile ligands, in which the displaced ligand remains attached to the complex upon analyte binding, have also been used. Examples of each of these approaches to metal-based chemosensors are discussed.

Keywords: Luminescence; Sensors

1. Introduction

Molecule-based chemosensors are molecules specifically designed to change their properties in response to the presence of other molecules. Conventionally, chemical sensor applications have exploited the bulk properties of solid-state materials such as metal oxides, which can exhibit, for example, changes in conductivity in response to the adsorption of oxidising or reducing gases to the surface of the material. The appeal of replacing bulk sensory materials with molecules derives from the ability to use chemical synthesis to prepare molecules that are designed to interact specifically with other molecules. Analyte-binding receptors can be carefully assembled using combinations of hydrogen bonding, electrostatics, covalent and coordinative bonding. Furthermore, the factors that influence molecule-based electronic properties are understood to the extent that

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* Corresponding author. Tel.: +1-604-822-1702; fax: +1-604-822-2847

E-mail address: mwolf@chem.ubc.ca (M.O. Wolf).

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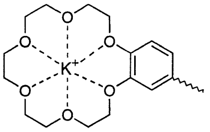
molecule–analyte interactions can be engineered to produce changes in readily monitored properties such as colour, photoluminescence and redox potential. These changes can, in turn, be interpreted in terms of sensor–analyte response. A major driving force behind the field of molecule-based chemosensors is the potential for miniaturisation of sensor technology down to the nanometer scale, where a single molecule could ultimately act as an individual sensor [1].

Molecular recognition is a well-developed field unto its own, studied largely out of interest in understanding the recognition processes in biological molecules such as enzymes. It is the combination of molecule–molecule interactions with changes in measurable properties which distinguishes molecular recognition from molecule-based chemosensing. Thus, molecule-based sensors combine analyte-binding or *receptor* function and analyte–response or *reporter* function, and the architecture of such sensors is often, but not necessarily, modular in nature.

The purpose of receptors is to provide fast and reversible binding of the analyte of interest, and molecular receptors for sensing purposes are designed with this function in mind. For example, cations are typically coordinated by crown ethers, cyclams and other arrays of lone-pair donors. Specificity is determined based on ion size and charge; for example, receptors **1** and **2** are specific for the ions shown and have been tethered to luminescent moieties to act as receptor modules in molecule-based sensors for these ions [2–5].



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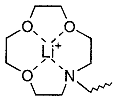

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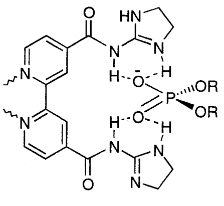
Anions are typically bound using sets of hydrogen bond donors and acceptors that are complementary to the acceptors/donors in the anion of interest [6,7]. For example, receptor **3** complexes phosphodiesters as shown and has been successfully incorporated into a luminescent ruthenium 2,2′-bipyridine complex that responds to these anions [8].



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Finally, small-molecule analytes such as CO, O_2, NH_3, H_2O and organic compounds that contain donor atoms can be coordinated by transition metals. Thus, the metal–ligand interaction has been utilised to develop transition-metal based small-molecule receptors, and this is the focus of this review.

In response to analyte–receptor binding, molecule-based sensors must undergo changes in readily monitored properties. While there are a variety of potentially variable properties to choose from, photoluminescence is particularly attractive for a number of reasons, which have been summarised well in a recent review by de Silva et al. [2]. From the standpoint of miniaturisation, the advantage of luminescence is that it avoids the problem of making electrical connections to extremely small sensors (i.e. individual molecules). Moreover, luminescence offers both high spatial and temporal resolution, as well as inherently large signal-to-noise ratios that can be further improved by designing the analyte-binding event to switch the sensor molecule between luminescent and nonluminescent forms. The most striking advantage of luminescence, however, is the high degree of sensitivity that can be achieved; in fact, luminescence arising from a single molecule can be detected via single photon counting. In addition to these advantages, the structural and environmental factors that influence molecular luminescence are well understood. This provides a rational basis for the design of molecule-based chemosensors that respond to analytes via changes in photoluminescence.

2. Factors that influence luminescence properties and the link to chemosensing

An understanding of the ways in which the emission properties of luminescent molecular units, called *lumophores*, can be manipulated is essential in order to design molecular sensors with analyte-dependent luminescence [9]. Here, a brief discussion of some of the environmental and chemical factors that can influence a lumophore's emission properties will be presented. Factors that can perturb the energetics of excited states are presented first, followed by a discussion of chemical processes that lead to the quenching of excited states. These are placed into the context of chemosensing through the inclusion of general examples of sensor motifs based on each manner of manipulating the emission properties of lumophores.

2.1. Stabilisation and destabilisation of the excited state

The ways in which an emissive excited state can become energetically stabilised or destabilised depend on the nature of the excited state. Bonding interactions between lumophores and other molecules or ions can alter the ordering of energy levels, which can result in switching of the lumophore between luminescent and nonluminescent forms. For example, molecules whose lowest energy excited states are n–π* in character, such as azaaromatics (e.g. phenanthroline), are typically nonemissive. However, the nitrogen lone pairs can coordinate cations such as H^+ and metal ions. The formation of Lewis acid–base adducts destabilises the n–π* state such that the order of the energy levels is reversed, and the lowest excited state becomes an emissive π–π* state. This type of OFF–ON luminescence switching has been used as the foundation of many luminescent molecule-based sensors for pH and metal cations [2].

Metal-centred and metal-to-ligand charge transfer (MLCT) excited states are susceptible to stabilisation or destabilisation through interactions that perturb the energetics of either the metal-based or ligand-based orbitals. Changes in the coordination environment of a metal centre affect the energetics of the metal-based orbitals, which in turn can alter the energy of metal-based, MLCT or ligand-to-metal charge transfer (LMCT) transitions involving these orbitals. The result can range from subtle shifts in emission energies to switching between emissive and non emissive forms, depending on the complexity of the exiced-state manifold of the complex. For example, luminescent Re, Ru and Os diimine complexes show strongly ligand-dependent luminescence properties, with both the colour of the emitted light and the sensitivity of the emission to temperature influenced by the nature of the ligands on the metal [10]. Moreover, the binding of molecules or ions to receptors built into the ligands involved in MLCT and LMCT transitions can alter the energetics of the ligand-based orbitals, and therefore induce changes in luminescence properties [2,7]. Numerous systems containing transition-metal diimine complexes with pendant anion receptors have been shown to display analyte-dependent luminescence because of electrostatic stabilisation or destabilisation of the emissive MLCT states.

2.2. Deactivation of the excited state

Lumophores that can be switched between emissive and nonemissive forms are attractive for chemical sensing because they offer the potential for extremely high signal-to-noise ratios. Excited-state deactivation can occur through typical nonradiative deactivation pathways, and the interaction of analyte species with the lumophore can sometimes alter these processes. For example, hydrated lanthanide complexes are weakly luminescent, but replacement of the coordinated waters by nonhydroxylic ligands results in dramatically increased luminescence intensities because the efficient nonradiative deactivation pathway provided by O–H stretching modes is removed [2,11]. For chemosensory applications, however, a more commonly utilised approach to excited-state deactivation is via the interaction of the lumophore with other moieties that have the ability to deactivate, or *quench*, the excited state via energy transfer and electron transfer.

Energy-transfer quenching occurs when the excited state's excitation energy is passed to another species in its ground state. Many luminescent sensors for oxygen gas are based on energy-transfer quenching of lumophores with triplet excited states; the presence of oxygen is signalled by a decrease in luminescence intensity [9,12]. More elaborate molecular sensor designs incorporate an energy donor and acceptor into the same molecule and function on the premise that the analyte-binding event modulates the distance between the donor and acceptor modules [2].

The other principle type of quenching process involves deactivation of the excited state by removal or addition of an electron from or to one of the excited state's singly occupied frontier orbitals. This photoinduced electron transfer (PET) leaves the lumophore in an oxidised or reduced state that is no longer emissive. Molecular sensors based on PET are built with a modular design, with lumophore and receptor modules typically separated by a spacer unit of well-defined length that allows for efficient electron-transfer processes. Several reviews are available that provide comprehensive listings of the important literature references in this well-developed field [2–6,13]. In typical PET-based chemosensors with the lumophore–spacer–receptor design, the analyte-binding event modifies the relative energies of the donor and acceptor energy levels such that the PET mechanism is switched ON or OFF upon coordination of analyte. This type of energetic perturbation forms the basis of many metal sensors that switch to a highly luminescent form in the presence of metal ions. For example, the complexation of metal cations by macrocyclic receptors, such as crown ethers, can modify the redox potential of the receptor such that it can no longer transfer an electron to the lumophore's excited state. In other cases, the analyte itself acts as the electron-transfer quencher, which results in luminescence being switched OFF in response to the presence of analyte. This approach has led to sensors for redox-active analytes ranging from open-shell metal ions to organic species such as quinones and nucleotides.

A less common approach to PET-based luminescence switching exploits the distance dependence of electron-transfer processes. In this approach, the binding of analyte to the receptor site causes a change in the distance between the lumophore and the quencher [14–17]. This distance modulation can result in analyte-induced ON–OFF or OFF–ON luminescence switching, depending on the design of the system.

3. Sensing based on analyte coordination to a metal centre

In order to design lumophores to respond to the presence of analyte species, it is important to establish an intimate link between the analyte-binding event and the luminescence properties of the lumophore. This can be achieved through careful consideration of the factors presented above and by selection of appropriate analyte–receptor moieties. As described above, sensor–analyte interactions should be fast, reversible and accompanied by an energetic perturbation in order to report the presence of analyte via a change in measurable properties. Metal–ligand coordinative bonding, by its very nature, fulfils these criteria. A variety of molecular sensors based on direct coordination of analytes to metal centres have been reported. To date, this aspect of the literature has not been reviewed in its own right, although several review articles include examples of sensors based on this premise [6,11,18–21]. Metal-based sensors that lack pendant receptors have been discussed briefly in a recent review [18]. As well, some examples of metals in both receptor and dual receptor–lumophore roles have been presented in an earlier review by de Silva et al. [19].

Part of the appeal of metal-based luminescent sensors is their photophysical versatility. Luminescent metal complexes that have the ability to coordinate analytes are natural candidates for molecule-based chemosensors because they can perform dual roles, as both the receptor and the lumophore in an all-in-one design. Metal-based lumophores are common and range from metalloporphyrins to late-metal diimine complexes to lanthanide complexes, which offer widely different luminescence characteristics and diverse coordination chemistry. The coordination of analyte to the metal can occur via occupation of a vacant coordination site or through displacement of weakly bound ligands. In either case, the resulting changes in the ligand environment around the metal influence the energetics of the metal-based molecular orbitals. These perturbations often lead to analyte-dependent changes in the absorption and luminescence properties of the complex, such as spectral shifts, but can also result in dramatic changes in luminescence intensity.

Alternatively, metal-based analyte receptors can be combined with organic lumophores to create coordination-based sensors with a modular design. By virtue of their ability to undergo electron-transfer processes, many open-shell transition metals are effective luminescence quenchers; this trait is often exploited to construct complexes with analyte-dependent luminescence properties. In some cases, the analyte-binding event simply modulates the distance between the organic lumophore and an intramolecular quencher, such as the metal centre. In other cases, the analyte itself is capable of either quenching the luminescence or switching off a quenching mechanism. Both approaches result in analyte-dependent changes in luminescence intensity that can be used to signal the presence of analytes.

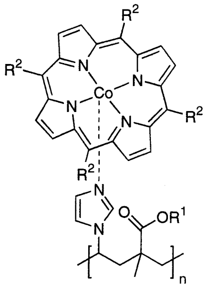
Here, the recent literature on molecule-based chemosensors whose photophysical response to analytes arises from direct metal-analyte coordination is reviewed. The literature is organised according to the nature of the analyte-binding event, i.e. coordination of analyte to a vacant site on the metal vs. coordination via displacement of weakly bound ligands, and is further subdivided based on the role that the metal plays, either as a dual purpose receptor-lumophore or as a receptor that influences a lumophore to which it is tethered.

4. Analyte coordination to a vacant coordination site

The simplest receptor design involves straightforward binding of the analyte species to a coordinatively unsaturated metal centre. Molecule-based chemosensors based on metal complexes with vacant coordination sites are common; many of these consist of complexes with polydentate ligands such as tren derivatives or macrocycles such as porphyrins and cyclams. In many cases, the metal plays a dual role as both receptor and lumophore, but the more common approach involves modular designs in which a metal acts as the receptor and the analyte-binding event influences an organic lumophore.

4.1. Metals as both receptor and lumophore

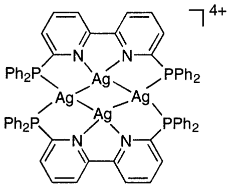
Complexes of macrocyclic ligands such as porphyrins and phthalocyanines are widely used as the basis of synthetic small-molecule receptors in studies on molecular recognition and chemosensing; only a cursory overview of these complexes is presented here since other reviews are available on this subject [21,22]. The planar nature of the ligand framework in general leaves the metal with empty coordination sites to which Lewis basic small molecules and anions can bind. Porphyrins and phthalocyanines are often used as synthetic small-molecule receptors in sensors based on nonphotophysical response [23], such as those that utilise quartz microbalances [24,25] and surface acoustic wave devices [26]. Metalloporphyrins have also been used as surface-tethered analyte receptors on luminescent CdSe films [27–29]. However, applications of metalloporphyrins are typically linked to their interesting photophysical and photochemical properties; [10,30] the complexes are intensely coloured, usually luminescent, and undergo a variety of energy- and electron-transfer processes. Many examples of sensors that use metalloporphyrin receptors rely largely on the colour changes that occur when the empty coordination sites on the metal are occupied by analytes. For example, a cobalt(II) porphyrin complex coordinated to an imidazole-functionalised polymer **4** reversibly binds oxygen to produce a large colour change [31].



4 R^1= *n*-octyl or 2,2,3,3,4,4,5,5-octafluoropentyl
R^2= *o*-pivalamidophenyl

Molecular imprinting techniques have been used to prepare Zn(II) porphyrin-doped polymers that show colour changes specifically in response to nucleobases [32]. Colorimetric sensor arrays based on metalloporphyrin dyes reported by Rakow and Suslick permit a wide range of coordinating organic solvents to be distinguished upon exposure of the sensor array to solvent vapours; [33] these arrays function without interference from water vapour and yield low detection limits (<100 ppb). Recent literature on porphyrin-based chemosensors with luminescence response has been predominantly focused on sensing oxygen gas [34–42]. Furthermore, a recent review [22] presents a variety of luminescent metalloporphyrins that bind analytes via cooperation of the metal and elaborate binding pockets built around the open coordination sites.

Cluster complexes with coordinatively unsaturated metal atoms have also been studied in light of their potential to act as luminescent chemosensors. In a recent example, a luminescent tetrametallic silver(I) bipyridyl phosphine cluster complex **5** shows luminescence that is sensitive to oxygen, coordinating solvents and certain other ligating species [43]. Addition of DMSO or MeCN to the cluster complex leads to an enormous decrease in luminescence intensity; the complex also reversibly responds to CO gas, but irreversibly to NO. The luminescence response arises from reorganisation of the cluster's core because of the addition of extra ligands to the coordination spheres of the metals.



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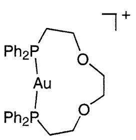

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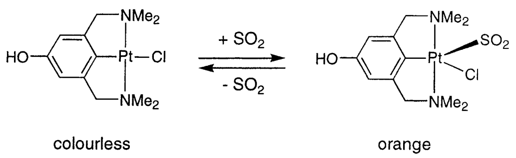
Luminescent gold complexes have also been presented as candidates for chemosensory applications. In a recent report, [44] a nonluminescent two-coordinate gold(I) bis(phosphine) loop complex (**6**) was described that switches to a highly luminescent form (yellow emission) upon coordination of triphenylphosphine to the unsaturated Au centre. Three-coordinate Au(I) phosphine complexes are generally luminescent, [45] which suggests that this complex might be used to report the presence of a variety of different analyte species. The improved chemical stability of the loop complex over other two-coordinate Au(I) complexes may make this complex particularly attractive for sensor applications.

Finally, the laboratory of van Koten has reported extensive work on organoplatinum(II) halide complexes such as **7** that contain a monoanionic bis(amino)aryl 'NCN' pincer ligand. These coordinatively unsaturated metal complexes are not luminescent, but their simple design and reversible colorimetric response to analyte in both solution and the solid state demand attention. As shown in Scheme 1, the four-coordinate metal centre rapidly and reversibly binds SO_2 via the sulphur atom to form a five-coordinate species, and the increase in coordination number is accompanied by a dramatic colour change from colourless to orange [46,47]. These Pt complexes have been incorporated into dendrimeric structures [48–50] and polymers [51] and show great promise as SO_2 sensors [49].

4.2. Metal-based receptors with organic lumophores

In the somewhat more complicated modular design, the metal functions as the receptor while the luminescence response arises from a (typically organic) lumophore that is covalently attached to the metal-based receptor. The metals involved are generally late transition metals with unfilled d-shells, such as Cu(II) and Co(II), and their ability to quench excited states via electron-transfer processes is exploited to achieve analyte-dependent luminescence response [2,13]. Organic lumophores abound, but those most commonly encountered in the molecular sensor literature [2,13] are based on polyaromatic hydrocarbons (pyrene, anthracene, naphthalene), acridine, coumarin and dansyl units, all of which are susceptible to luminescence quenching via electron transfer to appropriate electron acceptors. Closed-shell metal ions such as Zn(II) are also commonly used in conjunction with lumophores such as azaaromatics, whose emission is switched on upon formation of Lewis acid–base adducts. In these cases,



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Scheme 1.

the lumophore's response to the coordination of analyte to the metal centre arises from quenching mechanisms other than electron transfer.

In one approach, organic lumophores that are capable of coordinating to metal ions are employed. Analyte binding is accomplished through interaction with the coordinatively unsaturated metal centre and an additional receptor moiety tethered to the lumophoric ligand. (It should be noted that these experiments are typically performed in aqueous solution, and it is likely that the 'vacant' coordination sites on the metal are occupied by water molecules. However, since these ligands have not been intentionally included as part of the chemosensor design, this approach has been included here.) For example, a combination of the carboxylate-binding ability of Zn(II) and the reactivity of boronic acids towards hydroxyl groups has been utilised to create a receptor for sugar derivatives [52]. In this chemosensor, a boronic acid group is pendant to a phenanthroline unit, which serves a dual role as the ligand that anchors the boronic acids to a Zn(II) centre and as the lumophore. The binding of uronic acids, in particular, to the complex (via coordination to both the boronic acids and the metal centre) disrupts a luminescence quenching mechanism; the presence of uronic acids is, therefore, signalled by a significant increase in phenanthroline-based emission. In a similar approach, a copper(II) phenanthroline complex has been designed with a citrate binding site that contains two guanidinium groups plus the Cu(II) centre, as shown in Fig. 1 [53]. Again, the lumophore is the phenanthroline unit, and the binding of citrate to the guanidinium groups and the Cu(II) centre disrupts the quenching of the phenanthroline emission by the metal. The luminescence response of this complex has been successfully used to determine the amount of citrate in sports drinks.

5. Analyte coordination through displacement of weakly bound ligands

5.1. Metals as both receptor and lumophore

A considerable amount of effort has been focused on the use of luminescent lanthanide complexes in chemosensing applications. The metal-centred excited states of lanthanide complexes give rise to long-lived emission, particularly in the absence of hydroxylic ligands. In lanthanide-based chemosensor complexes, analytes typically bind to the metal by displacing weakly bound water molecules; this gives rise to a strong enhancement of luminescence because O–H stretching modes provide a powerful nonradiative deactivation pathway for lanthanide excited states. Because the f electrons involved in the photophysics are shielded by the d-shell electrons, lanthanide emission is relatively insensitive to environmental effects and changes in ligands. This tolerance to changes in ligands enables complexes to be prepared with a wide range of ligands, to provide high chemical stability and other desirable properties, without compromising the desired luminescence properties. Excellent reviews are available that discuss lanthanide-based sensors [2,11], so no effort is made here to summarise the literature on this topic. One example of particular note, however, involves a europium(III) complex with polymerisable ligands that was polymerised to form a molecularly imprinted polymer matrix specific for the detection of organofluorophosphorus nerve agents [54]. The luminescence response of prototype sensor devices containing this lanthanide-derivatised polymer permits quantitative detection of the hydrolysis product of chemical warfare agents at levels as low as 125 ppt.

5.2. Metal-based receptors with organic lumophores

Structural motifs such as cyclodextrins and calixarenes, commonly studied for their interesting host–guest chemistry, have also been adapted for application to luminescent chemosensing. Incorporation of lumophores and metal-coordination sites pendant to these guest-binding pockets has led to a number of complexes that show analyte-responsive photophysical behaviour. For example, the cyclodextrin depicted schematically in Fig. 2 contains a pendant dansyl-terminated diethylenetriamine group, which binds to Cu(II) via the three nitrogen atoms to form a complex that exhibits only

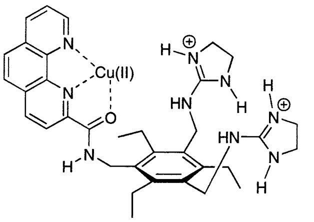

Fig. 1. A copper(II) phenanthroline complex containing two guanidinium groups with a citrate binding site.

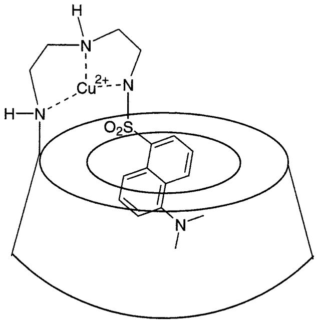

Fig. 2. A cyclodextrin with a Cu(II) binding pendant dansyl-terminated diethylenetriamine group.

weak dansyl-based luminescence because of electron-transfer quenching by the open-shell metal ion [17]. Addition of amino acids to the complex results in a significant increase in luminescence intensity due to displacement of the dansyl's amido group from the metal centre, which shuts off the quenching mechanism by increasing the distance between the lumophore and quencher. The cyclodextrin cavity appears to be involved in the binding process since L-alanine and L-tryptophan give rise to luminescence responses of different magnitude.

Fabbrizzi and coworkers have contributed several examples of Zn(II)-based small-molecule receptors that influence the emission of an intramolecular lumophore. In one example, a luminescent anthracene unit with pendant amines that can encapsulate a Zn(II) centre shows decreased luminescence in response to the binding of aromatic carboxylate ions to the coordinatively unsaturated Zn(II) centre [55,56]. The luminescence response arises from electron-transfer quenching between the aromatic groups and the anthracene when they are held close together in space by the metal centre. In another example, an anthracene unit with eight amino groups forms a dizinc(II) complex **8** that binds imidazolates as a bridging ligand between the metal centres, such that the imidazolate ring is π-stacked with the anthracene (Fig. 3) [57]. In this case, the anthracene luminescence is quenched by the imidazolate via electron transfer from the imidazolate anion to the photoexcited anthracene.

In a similar approach, an acridine lumophore with a pendant cyclam unit that binds Zn(II) has been used as a luminescent nucleoside receptor [58,59]. The open coordination site on the metal allows nucleosides to bind in such a way that the nucleoside and acridine interact with one another. The luminescence is significantly quenched in the presence of thymidine, whereas other nucleosides do not result in a large luminescence response. Thus, this sensor provides a selective response even without specific binding.

5.3. The hemilabile ligand approach to analyte coordination

In the context of chemical sensing, interactions between the analyte and metal should ideally be reversible. When a weakly bound ligand is displaced by an analyte, the displaced ligand can diffuse away from the metal after the analyte binds, which generally leads to irreversible metal–analyte interactions. However, it is possible to covalently tether the displaceable ligand to the metal via a multifunctional ligand that can bind via two (or more) donor atoms to prevent this departure. The simplest scenario involves a bidentate ligand with two different donors, one that binds strongly to the metal and one that binds weakly and therefore can be displaced by other coordinating species. Such ligands are described as *hemilabile* because half the ligand can undergo displacement from the metal while the other half remains firmly metal bound [60]. There are several reviews available on the subject of hemilabile ligands [61–63] that outline the motivations and provide detailed summaries of the diverse literature on this topic.

A generalised substitution reaction in which a hemilabile ligand competes for a coordination site with a small-molecule donor, A, is shown in Scheme 2. The labile donor is displaced yet remains in the vicinity of the metal centre. Thus, an equilibrium is established in which recoordination of the labile moiety is entropically favoured due to the chelate effect; the position of equilibrium, however, will naturally depend on the relative metal–ligand affinities. Ideally, the chelate complex can be regenerated if the concentration of competing small molecule A is decreased, and it is this promise of reversibility that is attractive for chemical sensing applications.

The first study in which hemilability was used in chemical sensing was reported by Dunbar and coworkers in 1992 [64]. They have extensively studied the reactions of carbon monoxide with cationic Rh(I) and Rh(II) complexes [65,66] that contain the hemilabile phosphine–ether ligand tris(2,4,6-trimethoxyphenyl)phosphine (TMPP). The Rh(I) monocarbonyl complex **9** shown in Scheme 3 reacts with CO, a process that is accompanied by absorption changes in both the visible and IR regions of the spectrum as well as a change in the metal's reduction potential. The reaction is reversible, and the response is selective for CO in the presence of O_2, CO_2, N_2 and H_2 under ambient conditions. Furthermore, the reversible response to CO is maintained when the CO-sensing complex is incorporated [64] into solid-phase thin films of zirconia glass prepared via the sol–gel process (chemical sensing using sol–gels has been recently reviewed [67–69]). Thus, this complex is a very promising molecule-based CO sensor.

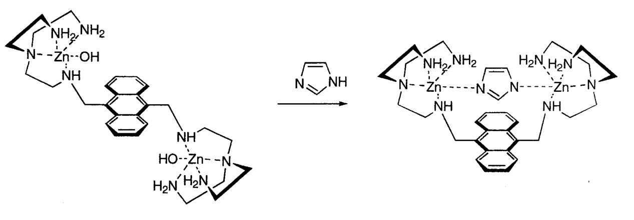

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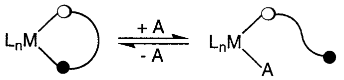
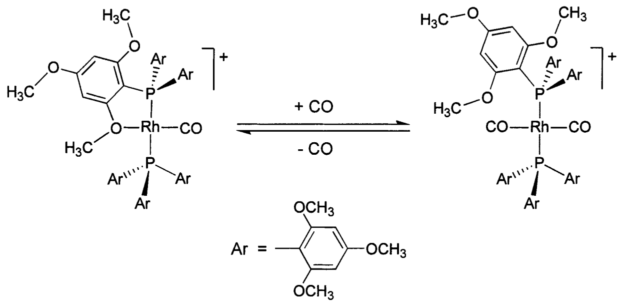
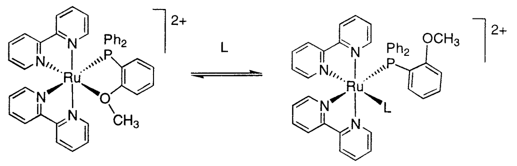
Fig. 3. Reaction of the dizinc(II) complex **8** with imidazole.



Scheme 2.



Scheme 3.



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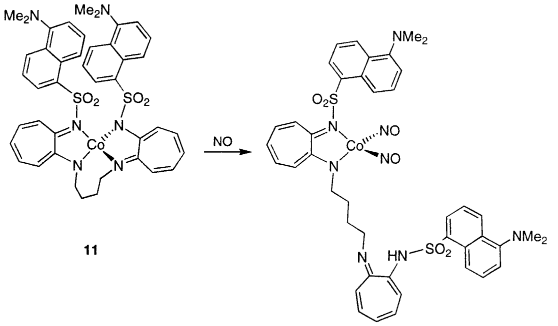
L = DMSO, $C_{12}H_{25}SH$, H_2O

Scheme 4.

In our group, we have developed Ru(II) bipyridyl complexes that react reversibly with sulphur donors such as thiols, sulphoxides and sulphides (Scheme 4) at a coordination site occupied by a hemilabile ligand [70]. These molecules respond to the binding of analyte via analyte-specific changes in the absorption and low-temperature emission spectra. For example, binding of DMSO results in a significant red shift in the emission spectrum, whereas thiols induce a slight yellowing of the emission. Complex **10** also binds water, with a concomitant red shift in both the absorption and low-temperature (77 K) emission spectra, which suggests that this species could be useful as a humidity sensor [71].

A metal-based small-molecule receptor **11** with luminescence response to nitric oxide gas was reported by Lippard and co-workers [15,16]. In complex **11**, depicted below in Scheme 5, two dansyl groups are held in close proximity to a Co(II) centre by virtue of the fact that the lumophores are covalently attached to chelating amido-imine ligands. In this arrangement, the dansyl groups are only weakly luminescent because of efficient electron transfer from the dansyl excited state to the open-shell metal. Exposure of the complex to NO results in replacement of one of the amido-imine chelates with two-coordinated NO molecules. Thus, one of the dansyl moieties is displaced from the metal such that the distant-dependent electron-transfer quenching mechanism is disrupted, and strong luminescence is observed from this dansyl group. The tether between the two amido-imine units is sufficiently long that, even if the coordinated NO molecules were to dissociate from the metal, recoordination of the second amido-imine unit is entropically disfavoured. Thus, in its present design, the complex is limited to irreversible sensing of analyte.



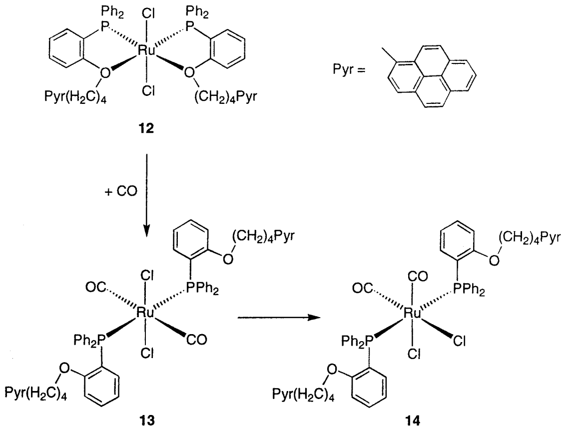
11

Scheme 5.

Our group has very recently shown that a ruthenium complex containing hemilabile phosphine-ether ligands that bear pendant pyrenyl groups (**12**) shows significant changes in its luminescence spectrum upon binding of carbon monoxide [72]. In this reaction, the initially formed *trans* dicarbonyl complex **13** isomerises thermally to the *cis* dicarbonyl **14** (Scheme 6). The luminescence spectra of these complexes (Fig. 4) show that a low energy emission band centred at 475 nm appears in both dicarbonyl complexes, which switches the emission colour from indigo-blue to blue-green. This change is due to formation of an intramolecular excimer, which can form because of the enhanced flexibility in the tether to the pyrene in these dicarbonyl complexes compared to **12**.

6. Summary

Examples of several classes of luminescent molecule-based chemosensors in which sensing is achieved via binding of analytes as ligands to metal receptors have been described here. Two general approaches are available: the metal complex may act as both receptor and lumophore; or, alternatively, a pendant lumophore coordinated to the metal receptor can provide the luminescence response. In addition, different binding



Scheme 6.

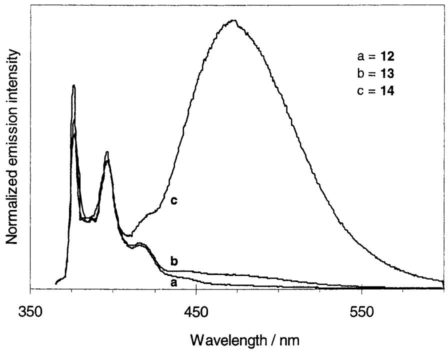


Fig. 4. Comparison of the emission from dilute solutions ($\sim 10^{-6}$ M) of: (a) **12**; (b) **13**; and (c) **14**. Excitation wavelength 350 nm.

scenarios are possible that differ in the nature of the binding site: analyte binding can occur at a vacant coordination site on the metal chemosensor or by displacement of a weakly bound ligand.

The range of analytes that has been detected using the approaches described here is broad, which demonstrates that molecular chemosensors may ultimately be used in many environmental, biomedical and industrial applications. It is important to recognise that significant challenges still remain, such as the optimisation of sensitivity and selectivity. The work discussed in this review illustrates that luminescence-based sensing is an effective approach to achieving improved sensitivity. An interesting approach to enhancing selectivity which has only begun to be explored in metal-based sensors is to utilise cooperative binding involving interactions between the analyte and both metal and a suitably designed pendant ligand. This is conceptually analogous to the high specificity achieved in the binding of certain enzyme substrates to metal cofactors. Challenges also exist in moving what has been learned about molecular chemosensors from solution to the solid state. Possible approaches include the development of polymer- or glass-supported chemosensitive materials. These approaches offer opportunities for integration of molecules with conventional optoelectronic and chip-based technologies.

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