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Chromo- and Fluorogenic Organometallic Sensors

Nicholas C. Fletcher and M. Cristina Lagunas

Abstract Compounds that change their absorption and/or emission properties in the presence of a target ion or molecule have been studied for many years as the basis for optical sensing. Within this group of compounds, a variety of organometallic complexes have been proposed for the detection of a wide range of analytes such as cations (including H^+), anions, gases (e.g. O_2, SO_2, organic vapours), small organic molecules, and large biomolecules (e.g. proteins, DNA). This chapter focuses on work reported within the last few years in the area of organometallic sensors. Some of the most extensively studied systems incorporate metal moieties with intense long-lived metal-to-ligand charge transfer (MLCT) excited states as the *reporter* or *indicator* unit, such as *fac*-tricarbonyl Re(I) complexes, cyclometallated Ir(III) species, and diimine Ru(II) or Os(II) derivatives. Other commonly used organometallic sensors are based on Pt-alkynyls and ferrocene fragments. To these *reporters*, an appropriate *recognition* or analyte-binding unit is usually attached so that a detectable modification on the colour and/or the emission of the complex occurs upon binding of the analyte. Examples of recognition sites include macrocycles for the binding of cations, H-bonding units selective to specific anions, and DNA intercalating fragments. A different approach is used for the detection of some gases or vapours, where the sensor's response is associated with changes in the crystal packing of the complex on absorption of the gas, or to direct coordination of the analyte to the metal centre.

Keywords Molecular Sensors, Molecular recognition, Organometallic, Fluorescence, UV-vis spectroscopy, Colorimetry

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Contents

1 Introduction

The colorimetric and fluorescent detection of localized molecular environments has become pivotal in the development of working sensor devices [1]. The diimine complexes of the late transition metals, many of which possess long lived excited states, have been in the vanguard of sensor design. Simple variation in their substituents not only allows the addition of a large variety of recognition sites but permits the photophysical properties to be tuned [2, 3]. As a result, a number of organometallic species of these relatively inert metals have found potential application in the detection of a wide variety of analytes, ranging from cations (including H^+), anions, gases and small organic molecules, all the way through to large biomolecules such as DNA.

As a general rule, a molecular sensor is comprised of two sections, usually located in two distinct domains. One part is employed in the *recognition* of the target analyte. Through the considerable efforts within the fields of supramolecular and host–guest chemistry, suitable recognition units have been designed for the detection of a wide variety of materials. The second key unit is the *indicator* or *reporter* that, upon a successful recognition event, undergoes a detectable change such as in the colour, the fluorescence or even the redox potential. One of the most extensively studied systems is the tris(2,2′-bipyridyl)ruthenium(II) cation as a consequence of its unique combination of chemical stability and emissive behaviour. There are numerous examples where this simple moiety has been incorporated into larger sensing devices, and will not be considered further in this chapter [4]. However, it is noted that many of the ligand systems explored with this stalwart of coordination chemistry have also been incorporated into a range of other organometallic luminescent platforms, such as the *fac*-tricarbonyl rhenium(I) moiety, which possesses a long lived triplet metal-to-ligand charge transfer (^{3}MLCT) state. Cyclometallated iridium(III) complexes have also drawn considerable recent attention [5], as they offer the possibilities of tuning emissive states by ligand modification opening routes to red, green and even blue fluorescent materials, as well as larger quantum yields in comparison to the analogous Ru(II) complexes. Attention is also drawn to the acetylene complexes of platinum which have undergone considerable developments in recent years [6].

The objective of this chapter is to draw attention to a number of recently reported organometallic complexes which detectably change their optical properties in the presence of a target analyte. While every effort has been made to ensure that the chapter is as inclusive as possible, a degree of selectivity has had to be undertaken.

2 Cation Sensors

2.1 Rhenium(I) Carbonyl Complexes

Tricarbonyl Re(I) complexes $[\mathrm{Re(CO)_3L}]^+$, where L is usually a bipyridine ligand, are often used as optical sensors based on their low-lying MLCT excited states [$d\pi(\mathrm{Re}) \rightarrow \pi^*(\mathrm{L})$]. A common strategy for cation sensing is the attachment to L of pendant macrocycles, such as crown ethers. In order to ensure a good electronic communication between the cation-binding macrocycle and the reporter Re centre, Lazarides et al. [7] have recently developed ditopic ligands derived from 5,6-dihydroxy-1,10-phenanthroline where pendant crown ether groups are directly linked to the phenanthroline fragment (**1a**, **1b**; Fig. 1). A limitation of the system was found to be the poor donor ability of the O atoms directly connected to the electron-withdrawing phenanthroline–Re moiety, which resulted in unexpected low binding constants for K^+. However, **1a** and **1b** both showed strong binding to Ba^{2+}, which was easily detectable through the quenching of the ^{3}MLCT luminescence band (and a slight red-shift). The incorporation of soft donor atoms such as S or Se in the pendant groups allows for specific binding of soft metal cations. For example, Yam et al. [8] have achieved highly selective sensing of Pb^{2+} and Hg^2 using complexes **1c** and **1d**, respectively (Fig. 1). In this case, spectral changes were observed both in the UV–Vis and luminescence spectra of the compounds. In particular, a significant enhancement of the ^{3}MLCT luminescence intensity (and a slight red-shift) was observed upon addition of the metal cations in acetonitrile. An alternative approach to facilitate effective electron communication between the pendant group and the reporter unit is the incorporation of conjugated spacers such as the alkene or alkyne moieties used to link azacrown groups to the pyridyl ligands in complexes **1e** and **1f** (Fig. 1) [9, 10]. The UV–Vis absorption spectra of these

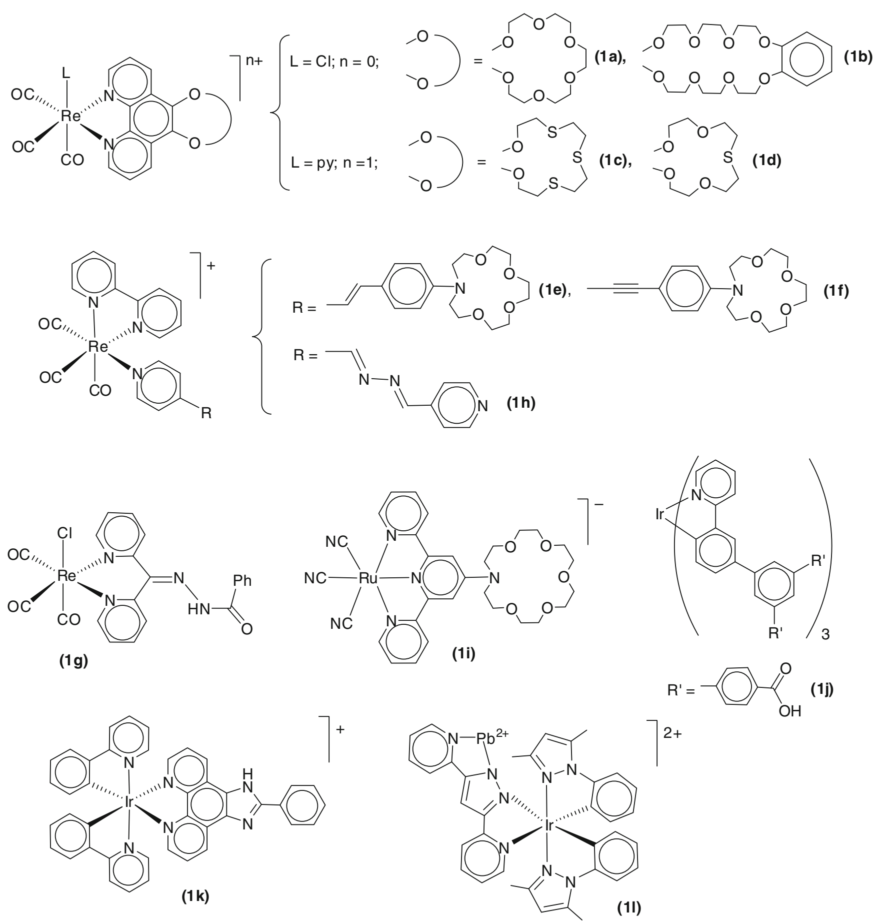

Fig. 1 Examples of Re, Ru and Ir complexes with pendant functionalities suitable for cation binding

compounds are dominated by strong intra-ligand charge transfer (ILCT) transitions localized on the pyridyl ligands (i.e. charge is transferred from the azacrown N atom to the ethenylpyridyl or ethynylpyridyl group) which hide the typical MLCT band. On protonation of the azacrown nitrogen, or complexation of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} or Ba^{2+} into the macrocycle, the ILCT band shifts to lower wavelength with the magnitude of the shift being dependent on the cation. Recent work also include the development of pH-sensitive systems, such as *fac*-[Re(CO)$_3$(di-2-pyridylketonebenzoylhydrazone)Cl] (**1g**; Fig. 1), whose UV–Vis absorption spectrum has been shown to be very sensitive to the addition of acid or base, with acid concentrations as low as 10^{-9} M detected in DMF solution. This behaviour is attributed to the compound's ability to form strong H-bonding interactions with surrounding molecules through the amidic hydrogen atom [11]. The proton acceptor properties of the imine and/or pyridine N atoms in the ligand 4-pyridinecarboxaldehydeazine have also been exploited to prepare the pH-sensitive luminescent Re(I) complex **1h** (Fig. 1) as well as dinuclear Re^IRe^I and Re^IRu^{II} analogues [12].

2.2 Ruthenium(II) and Osmium(II) Complexes

The complex $[Ru(bpy)(CN)_4]^{2-}$ and its analogues are, like the Re-carbonyl species discussed above, typical MLCT [$d\pi(Ru)\rightarrow \pi^*(bpy)$] chromophores that can be used as optical molecular sensors, usually exploiting the ability of the cyanide ligands to coordinate metal cations. For example, the interaction of $[Ru\{4,4'\text{-di}(^{tert}\text{butyl})\text{-}2,2'\text{-bpy}\}(CN)_4]^{2-}$ with a variety of metal cations, such as Li^+, Na^+, K^+, Cs^+, Ba^{2+} and Zn^{2+}, in acetonitrile results in a blue-shift of the ^{1}MLCT absorption and the 'switching on' of strong ^{3}MLCT luminescence. The energy and intensity of the emission depends on the nature of the cation present, with λ_{em} varying from 646 nm (Cs^+) to 537 nm (Zn^{2+}) and the highest quantum yield (0.07) obtained for Ba^{2+}. Structural studies using the less soluble analogue $[Ru(bpy)(CN)_4]^{2-}$ showed that both 'end-on' and 'side-on' coordination of CN occurs, depending on the size and charge of the cation [13]. The rich luminescence properties of $[Ru(bpy)(CN)_4]^{2-}$ have also been used to design interesting logic gates responding to two chemical stimuli (acid and base), based on the self-assembly of the Ru(II) complex with a naphthyl-substituted dendritic host [14]. Addition of a pendant azacrown ligand to $[Ru(terpy)(CN)_3]^-$ has resulted in a new water-soluble Ru(II) chromophore (**1i**; Fig. 1) which exhibits selective cation-binding behaviour (through the azacrown pendant) and pH-sensitivity (through protonation of the cyanide ligands). The complex has been shown to be a good candidate for sensing subtle humidity changes and to serve as a mobile-phase additive in high-performance liquid chromatography (HPLC) for the separation of alkali and alkaline-earth metal cations, as well as amino acids [15]. The cation-binding properties of a Ru(II)-carbene derivative with a benzo-15-crown-5 pendant have also been reported [16].

Cyano-Os(II) complexes can also be used as cation sensors in a similar manner as their Ru analogues. Thus, $[OsL_2(CN)_2(N\text{–}N)]$ (L is PPh_3, PMe_3 or DMSO) containing a variety of phen and bpy (N–N) ligands have recently been shown to act as luminescent sensors towards Zn^{2+} through ion binding of the cyano ligands [17].

2.3 Iridium(III) Cyclometallated Complexes

There are numerous instances where the MLCT phosphorescence of cyclometallated Ir(III) complexes is exploited for sensing applications. In a recent example, the emission intensity of the water soluble Ir complex **1j** (Fig. 1) has been shown to increase with an increase in pH, in accord with the degree of ionization of the carboxylic acid in the ligand. Addition of metal cations, however, quenched the luminescence, with a more significant change found for divalent ions Mg^{2+}, Cu^{2+} and Hg^{2+}, compared to monovalent alkali cations [18]. Derivatives containing imidazo-phenanthroline units, such as **1k** (Fig. 1) are also sensitive to the addition of H^+, possibly through interactions with the imidazolyl group, although these compounds have been mainly applied in anion sensing [19]. In another recent example (**1l**; Fig. 1), the cation-binding 3,5-di(pyridyl)pyrazole unit was used to preferentially bind Pb^{2+} vs Hg^{2+}, Ca^{2+} or alkali cations. The sensing of Pb^{2+} is based on the significant quenching of the room-temperature phosphorescence upon forming a 1:1 adduct with the Ir(III) complex, and can be performed in acetonitrile solution or by supporting the Ir(III) compound on a solid which can then be put in contact with an aqueous solution of Pb^{2+}. The latter provides the basis for a convenient detection device [20].

2.4 Ferrocene-Based Sensors

Although more often used as electrochemical sensors, ferrocene (Fc) derivatives can also act as optical sensors because their UV/Vis absorption properties can be readily modified upon binding of guests near the Fc moiety. This is usually achieved through perturbation of the characteristic low energy MLCT transition of ferrocene (at ca. 400–500 nm). Often dual sensors with combined electrochemical and optical responses are prepared, although only changes in the optical properties of the compounds will be discussed herein. Fc sensors are also particularly versatile because it is relatively easy to introduce a large variety of binding groups and functionalities on the cyclopentadienyl (Cp) ligands. For example, the doubly functionalized colourless Fc derivative **2a** (Fig. 2) can bind F^- through its urea fragment, and K^+ via the crown ether. Addition of F^- produces a yellow compound in acetonitrile, but the colour is quenched by the subsequent addition of K^+. This 'on–off' switching effect sets the basis for a logic gate [21]. Basurto et al. [22] have prepared a family of multi-functionalized Fc derivatives (e.g. **2b** and **2c**, Fig. 2) showing significant spectral changes upon addition of a variety of metal ions (e.g. Cu^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, Al^{3+} and Ag^+) as well as several anions, including the selective naked-eye colorimetric detection of Cu^{2+}. Fc ligands with diamino–diimido functionalities have also been proposed for the combined potentiometric/spectrophotometric detection of Cu^{2+} [23]. Diferrocenyl derivative **2d** (Fig. 2) allows naked-eye detection of Mg^{2+} and shows selective UV/Vis spectral changes towards this cation, while not responding to Ca^{2+} or alkaline metal ions. The metal-sensor interaction is believed to occur through the C=N–C group with no participation of the OH group [24]. Analogous Mg^{2+} detection properties have been also described for the related pyridine derivative **2e** [25], and the triferrocene complex **2f** [26], whereas Fc-ruthenocene derivatives (e.g. **2g**) act as selective

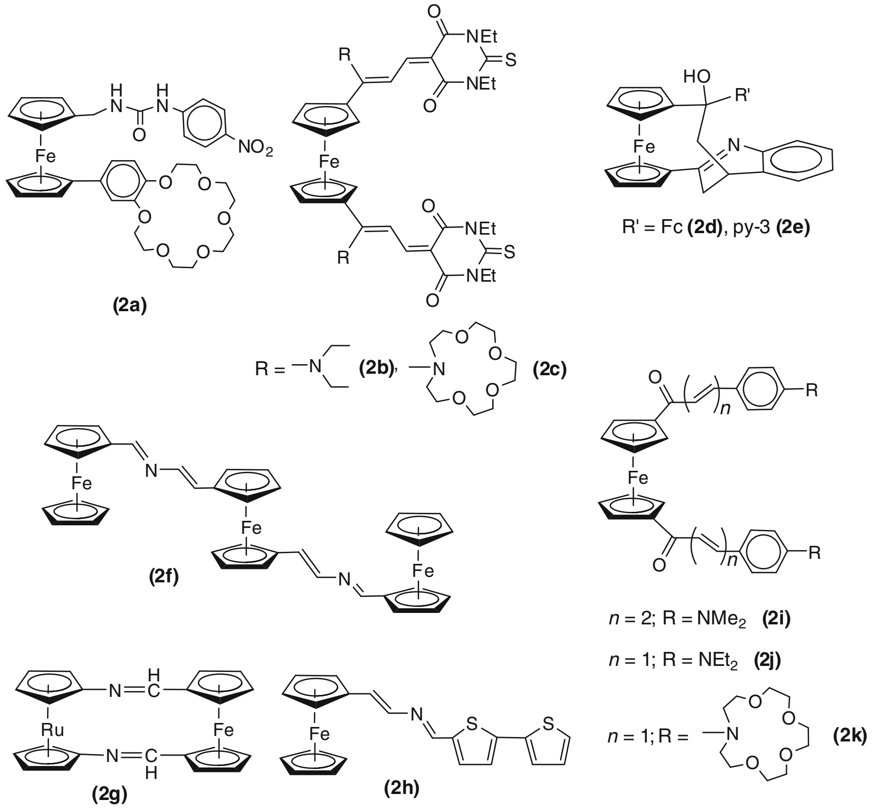

Fig. 2 Examples of ferrocene (Fc) derivatives used for cation sensing

naked-eye sensors towards Zn^{2+} in preference to many other mono- and di-valent cations (Fig. 2) [27]. In the two latter complexes, metal coordination is assumed to occur mainly through the aza-N atoms. The introduction of S-donor groups in this type of ligands (e.g. **2h**, Fig. 2) allows the selective detection of soft metals, such as Cd^{2+}, Hg^{2+} and Pb^{2+} [28, 29]. A series of other Fc-ruthenocene derivatives with interesting cation-sensing properties have also been reported [30, 31].

Despite the fact that Fc units normally act as fluorescence quenchers, it is possible to prepare fluorescent Fc derivatives that respond to the presence of guests. Thus, it has been shown that the absorption and emission spectra of compounds **2i**–**2k** (Fig. 2) change significantly in the presence of Ca^{2+} or Ba^{2+} but remain largely unchanged on addition of Li^{+}, Na^{+} or K^{+}, with the main metal binding sites located at the carbonyl group (**2i, 2j**) or azacrown (**2k**) groups. The detection ability of the compounds is, however, limited by the fact that the fluorescence intensity does not change monotonically with the concentration of the metal ion, which is attributed to the formation of various species with different stoichiometries in solution [32–34]. Analogous Fc derivatives with only one arm are not fluorescent but show UV–Vis spectral changes on addition of Ca^{2+} [35]. Ferrocene derivatives containing anthracene groups also act as cation sensors through enhancement of the structured fluorescent band of the anthracene moiety on metal complexation [36, 37].

2.5 Platinum(II) Complexes

In recent years, Pt(II) alkynyl terpyridine complexes have been shown to be versatile ion sensors [6]. For example, complexes with amino–alkynyl ligands (**3a**; Fig. 3) act as pH sensors, derivatives with crown ether pendants (**3b**; Fig. 3) have been used as sensors for mono- and di-valent cations, such as Li^+, Na^+, Mg^{2+}, Ca^{2+}, Cd^{2+} or Zn^{2+}, and analogous compounds containing flavones as pendant ligands have shown selective binding towards Pb^{2+} [38–42]. The origins of the changes observed in the absorption and emission spectra vary, with some systems showing switching between different excited states in the Pt(II) complex on ion binding. The related dinuclear calix[4]crown complex (**3c**; Fig. 3) also shows marked luminescence enhancement on cation binding, with a more selective response towards K^+ [43]. The supramolecular Pt rectangle (**3d**; Fig. 3) has been proposed as an optical sensor for Ni^{2+}, Cd^{2+} and Cr^{3+} in solution. The UV–Vis spectrum of the rectangle shows

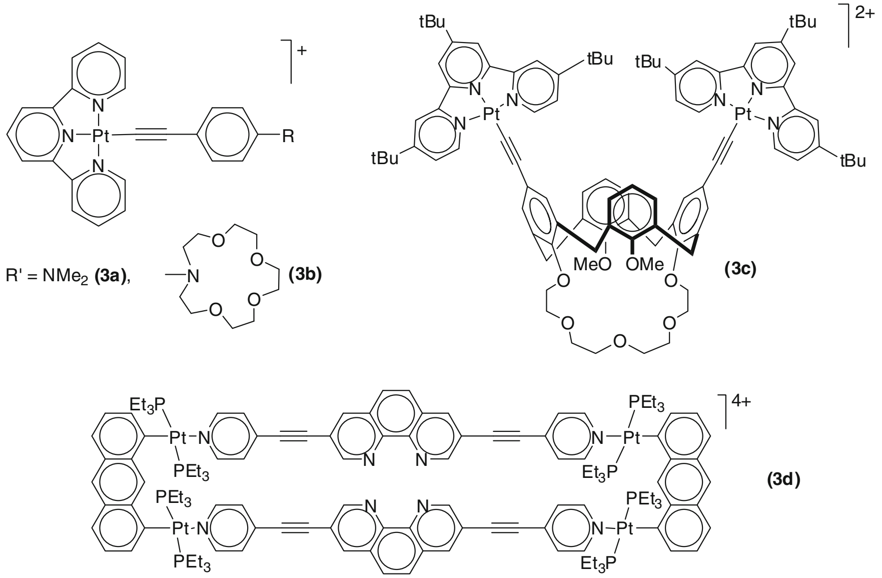

Fig. 3 Examples of Pt(II) complexes used for cation sensing

significant changes in the presence of the cations, which coordinate to the phenanthroline units without disturbing the supramolecular structure [44].

2.6 Gold(I) Complexes

The tendency of Au(I) and other d^{10} metals to form metal–metal interactions is often at the origin of intense emission, which has been exploited to prepare cation sensors; e.g. the emission can be switched ‘on’ by favouring the formation of metal–metal contacts upon ion coordination. This approach has been successfully applied by Yam et al., who used dinuclear Au(I) complexes containing ligands, such as calix[4]crown, crown ether or alkynyls, capable of trapping an additional metal ion and concomitantly altering the emission of the compounds by shortening significantly the Au–Au distance (e.g. **4a** and **4b**; Fig. 4) [45–48]. Recent work in related digold(I) complexes with alkynyl binding units has shown that cation binding can lead to complicated dimeric structures [49, 50]. Interestingly, Yam et al. have combined the binding and optical properties of Au(I)-alkynyls with the photoisomerization of azobenzene moieties in a macrocyclic complex, the conformation

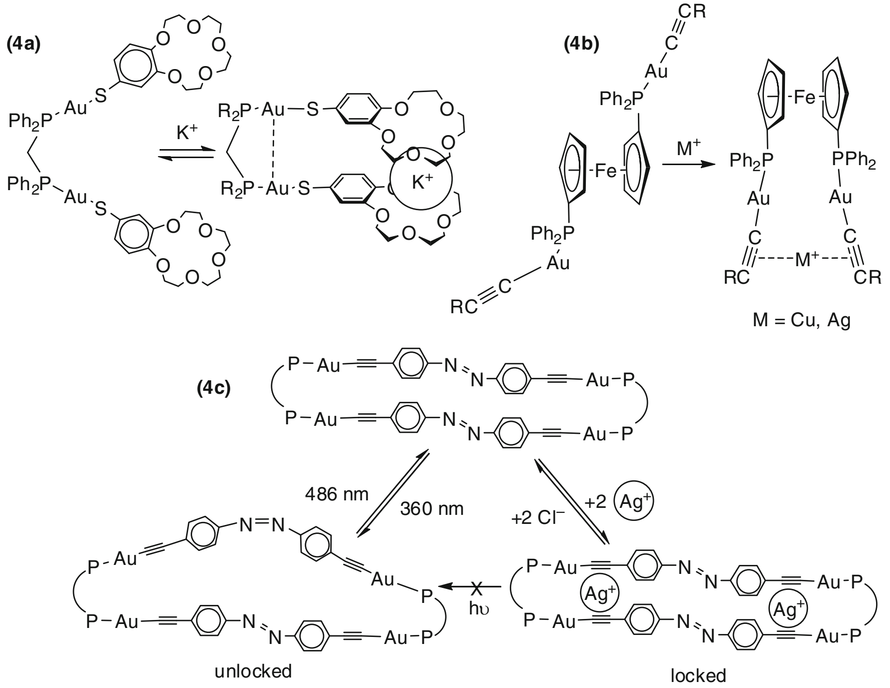

Fig. 4 Examples of applications of Au(I) complexes in optical sensing

of which can be controlled by addition or removal of Ag(I), thus setting the basis for a dual-input molecular logic photoswitch (**4c**, Fig. 4) [51].

3 Anion Sensors

3.1 Rhenium(I) Carbonyl Complexes

The Re(I) tricarbonyl moiety, in combination with pyridyl ligands, has led to a number of both neutral and charged species [52]. Sloan et al. initially isolated a self-assembled Re(I)–Pd(II) square (**5a**; Fig. 5) which demonstrated an increase in emission with the inclusion of ClO_4^- within the cavity and a binding constant of

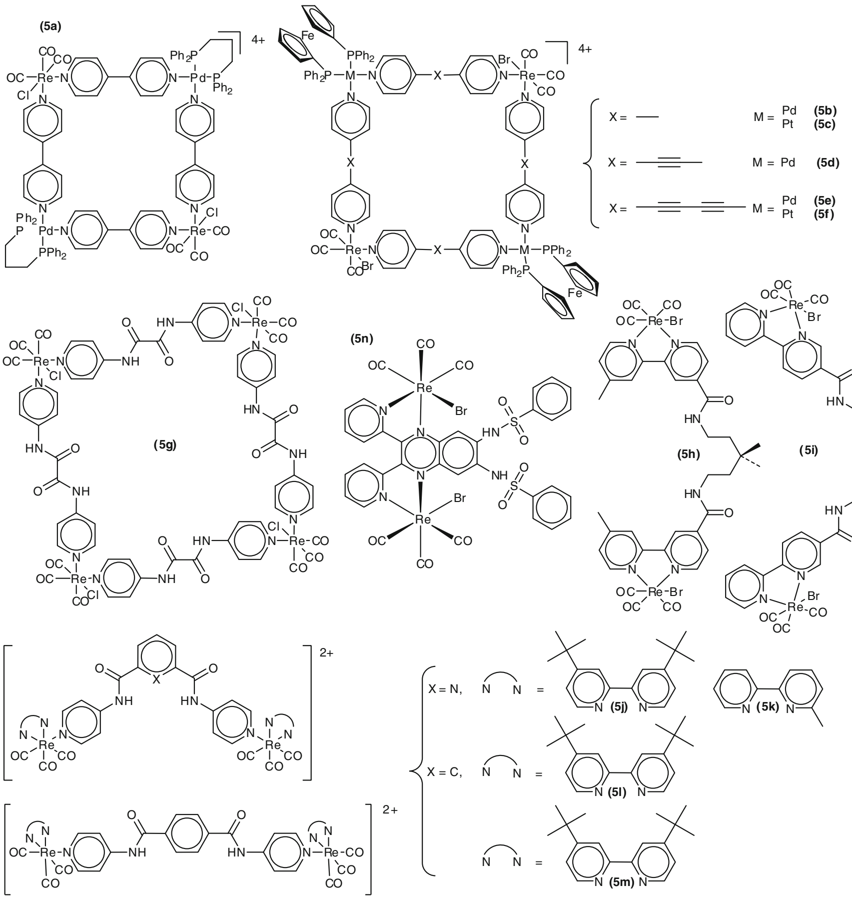

Fig. 5 Multimetallic Re(I) complexes suitable for anion binding

660 M^{-1} [53]. The much larger and rigid cavities (**5b–5f**; Fig. 5) from the Lees group showed an unusual change in their luminescence on the introduction of BF_4^- and PF_6^- anions, initially with a dramatic decrease in the observed fluorescence, followed by a significant increase. It is noted that there was no observed change with ClO_4^-, OAc^- and OTf^- [54]. More recently the neutral molecular square (**5g**) reported by Tzeng et al. has shown colorimetric changes on the introduction of a range of inorganic anions with selectivity for F^- over CN^- and OAc^-, and no perturbation observed for Br^-, PF_6^-, BF_4^-, ClO_4^-, NO_3^- or HSO_4^- [55].

The neutral dimetallic complex (**5h**; Fig. 5) reported by Beer et al., which demonstrated reasonable affinities for $H_2PO_4^-$ in ^1H NMR titration studies [56], inspired a recent study from Pelleteret et al. They have recently reported a series of neutral bimetallic Re(I) complexes (**5i**; Fig. 5), bridged by a flexible ethylene glycol diamide chain [57, 58]. This complex shows a significant increase in fluorescence upon the introduction of $H_2PO_4^-$ in non-protic solvents, which appears to arise from the removal of intra-molecular hydrogen bonds between the metal carbonyl and the free amide by the competitive oxo-anion. A series of structurally similar dinuclear luminescent Re(I) tricarbonyl anion receptors, featuring amide-type anion binding sites (**5j–5m**; Fig. 5) have also been shown to display outstanding sensitivity and selectivity toward a variety of anionic species [59, 60]. The intensity of these highly emissive positively charged species was significantly quenched by as much as 10%, even in the presence of only 10^{-8} M CN^- or F^- anions. The bis (sulfonamide) complex **5n** (Fig. 5) also exhibits considerable colorimetric change on the introduction of F^-, CN^- and OAc^-, attributed to a de-protonation which is exacerbated by the Lewis acidity of the metal and can be used to modulate the amidic pK_a [61].

Building on the ability of pendant cation receptors described above, the emission intensity of Re(I) complexes with pendant crown-ether groups (**6a–6c**; Fig. 6) was shown to increase on the addition of OAc^- with a concomitant 5 nm hypsochromic shift. The observed stability constants were larger when a K^+ ion sits within the macrocycle [62]. Similarly, the calix[4]arene appended complex **6d** (Fig. 6) demonstrates a selectivity for OAc^- with a marked revival of the quenched emissive behaviour on the introduction of the anions [63]. In another example, the inclusion of the positively charged pseudorotaxane thread within a macrocyclic complex (**6e–6h**; Fig. 6), assembled around a Cl^- ion, resulted in a significant enhancement in the fluorescence intensity [64]. This may be as a consequence of the increasing rigidity of the complex upon the interaction with the anion. This was further exemplified with a stoppered rotaxane thread (**6i**, Fig. 6), where removal of the templating anion, and subsequent replacement with Cl^-, NO_3^- and, significantly, HSO_4^- in acetone gave a similar increase in the quantum yield [65]. A couple of charged Re(I) complexes (**6j** and **6k**; Fig. 6) have been shown by Lo et al. to recognize F^-, OAc^- and $H_2PO_4^-$ with pK_s values ranging from 3.53 to 4.94 in acetonitrile [66]. While the anion binding properties of **6k** can be reflected by changes in the fluorescence, complex **6j** shows perturbations in both the absorption and emission spectra.

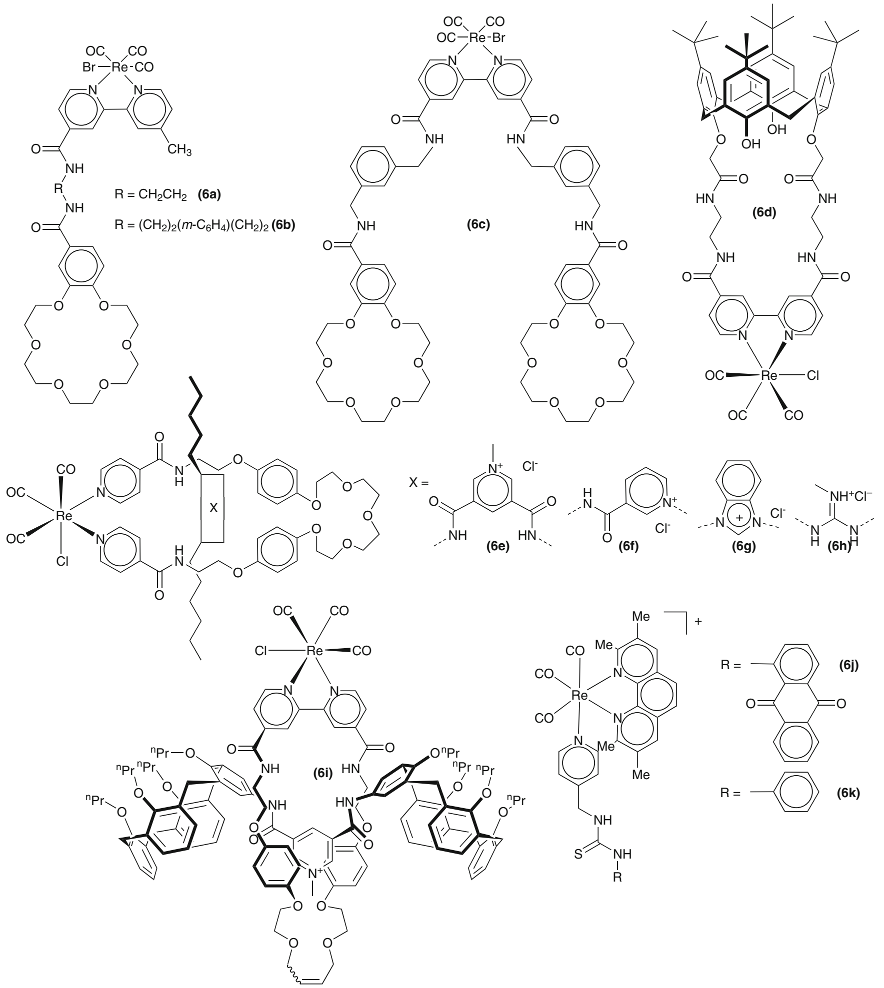

Fig. 6 Re(I) complexes with appended binding domains for anion recognition

3.2 Platinum(II), Ruthenium(II) and Iridium(III) Complexes

In recent years, several other organometallic fluorogenic centres have been considered for inclusion in anion sensing materials. Two Pt(II) terpyridyl alkynyl complexes (**7a** and **7b**, Fig. 7) show a dramatic colorimetric response to F^-, OAc^- and $H_2PO_4{}^-$, arising from interaction of the phenolic proton with the electronegative anion, and perturbation of the ligand-to-ligand charge transfer. Complex **7b** shows selectivity for F^- due to complete de-protonation [67]. In addition, complex **7a** has a considerable quenching in fluorescence on the addition of these anions. Similarly, a series of Ru(II) alkynyl complexes (**7c**–**7g**; Fig. 7) show a dramatic

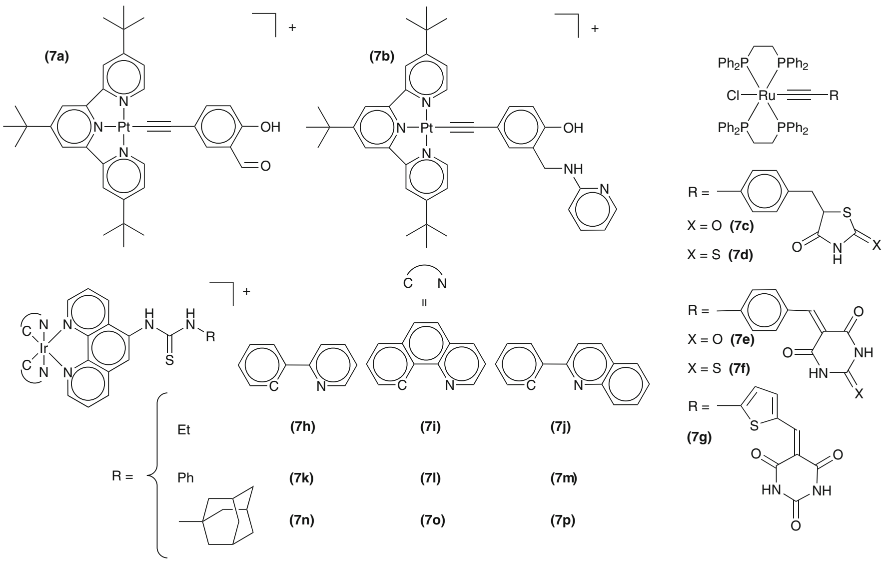

Fig. 7 Pt, Ru and Ir complexes with anion recognition behaviour

colour change, visible to the naked eye, on the addition of a range of anions including OAc^-, $H_2PO_4^-$, HSO_4^-, Cl^- and Br^-, although selectivity for F^- is evident, and there is a dependence on the electron density on the appended functional group [68]. Bucking this trend, a series of luminescent cyclometallated Ir(III) poly-pyridine thiourea complexes (**7h–7p**; Fig. 7), have shown selectivity for OAc^- over both F^- and $H_2PO_4^-$ [69]. The thiourea moieties of the complexes permit a 1:1 stoichiometry with the anion, as demonstrated by a significant quenching of the emissive ^{3}MLCT state. This behaviour appears to be independent of the appended functional groups.

3.3 *Ferrocene-Based Sensors*

It has already been noted that Fc complex **2a** gives a colorimetric change in the presence of F^- [21]. In addition to the electrochemical response [70, 71], the attachment of suitable chromophores/fluorophores to Fc has permitted optical responses to anions. This was initially demonstrated by Beer et al., who showed that the inclusion of $H_2PO_4^-$ in a cleft between a Ru(II) and two Fc groups (**8a**; Fig. 8) induced a significant increase and a 30 nm red-shift in emissive behaviour [72]. In the structurally similar Fc and cobaltocinium complexes (**8b** and **8c**; Fig. 8), the rate of the quenching energy transfer between the two metal centres could be perturbed by the inclusion of Cl^- in the intra-metallic cavity, resulting in a significant switching of the Ru MLCT based fluorescence [73]. The

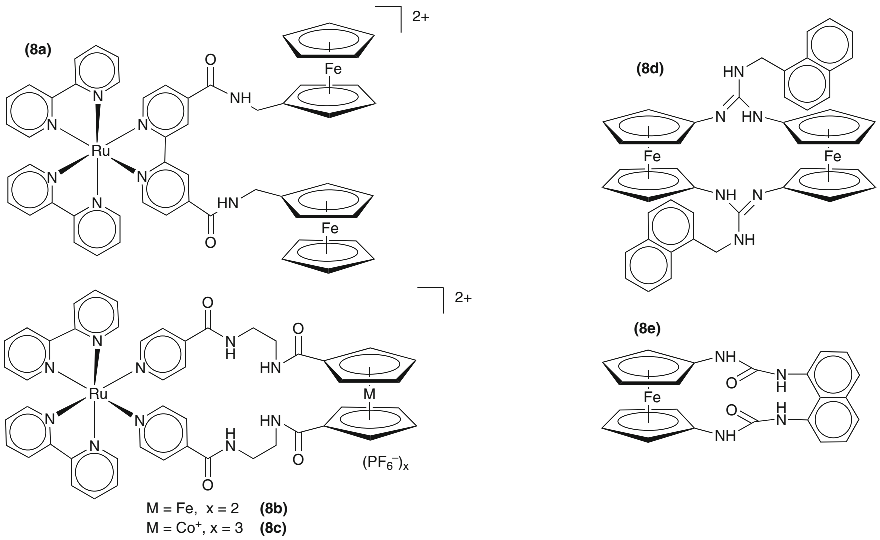

Fig. 8 Examples of ferrocene (Fc) derivatives used for anion sensing

guanidinoferrocene receptor (**8d**; Fig. 8), in addition to potentiometric detection of F^{-}, OAc^{-}, HSO_4^{-} and $H_2PO_4^{-}$, can act as a fluorescent chemosensor for Zn^{2+}, Ni^{2+} and Cd^{2+} metal ions. Furthermore, proton induced complexation provides a versatile means of sensing selectively NO_3^{-} via fluorescence quenching [74]. A urea centred complex (**8e**; Fig. 8) with a weak naphthalene emission when excited at 310 nm undergoes a 13-fold enhancement on the introduction of F^{-}, and a weaker, but significant response to $H_2PO_4^{-}$ [75].

4 Small Molecule Detection

4.1 Detection of Gases and Volatile Organic Compounds

The optical detection of vapours or gases by metal complexes often requires the sensor to show a response in the solid-state (i.e. detection takes place either by crystals of the complex, or by the compound supported on a solid matrix, cast as a film, etc.). Changes of the optical properties of the sensor upon absorption of the analyte are related to (1) quenching of the sensor's luminescence (e.g. by O_2), (2) disruption/modification of non-covalent interactions in the crystal packing of the sensor (e.g. H-bonding, π–π stacking, metal–metal contacts), and/or (3) change of the coordination environment of the metal centre (e.g. through coordination of the analyte to the metal). Although a porous sensor structure is not a pre-requisite, a relatively 'open' and flexible crystal packing favours the inclusion of the volatile and its interaction with the sensor.

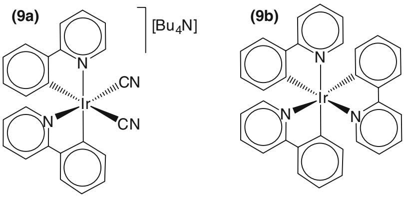

Fig. 9 Ir(III) complexes used for O_2 sensing

Detection of dioxygen is often based on the quenching of the ^{3}MLCT emission of d^6-metal complexes. In a recent example, cyclometallated compounds [Bu$_4$N][Ir(ppy)$_2$(CN)$_2$] (**9a**) and [Ir(ppy)$_3$] (**9b**; Fig. 9) dissolved in poly((*n*-butylamino) thionylphosphazene) polymer films have been shown to have high sensitivity to oxygen quenching [76]. Detection of SO_2 has been achieved using Pt(II) complexes with N,C,N′-pincer ligands which, in their crystalline state, are able to coordinate reversibly the gas giving rise to a colour change. Based on this process, multimetallic dendritic sensors were also developed [77]. Coordination of ethylene to Pd(II) or Pt(II) square planar complexes has recently been applied to prepare a colorimetric ethylene detector based on a 2,9-di-*n*-butylphenanthroline Pd(II) complex supported on silica [78].

The optical properties of Pt(II) complexes are often associated with the formation of Pt^{II}–Pt^{II} stacked structures [79]. Thus, the well-known intense colours and vapochromic properties of complexes [Pt(CNR)$_4$][M(CN)$_4$] (M is Pt, Pd; R is alkyl or aryl) are attributed to the presence of extended metal–metal chains of alternating anions and cations [80, 81]. The inclusion of vapour guests by the solids gives rise to colour changes (and/or changes in emission) which are mainly related to disruption of the metal–metal interactions, but also to changes in other non-covalent contacts throughout the structure. In recent years new analogues have been prepared and applied in novel sensing devices [82, 83], including humidity sensors [84]. Mann et al. [85] have shown that thermal re-arrangement of [Pt(*p*-CN–C_6H_4–C_2H_5)$_4$][Pt(CN)$_4$] also yields the vapochromic isomer *cis*-[Pt(*p*-CN–C_6H_4–C_2H_5)$_2$(CN)$_2$], whose structure also consists of linear Pt^{II}–Pt^{II} chains. Exposure of the crystalline solid to aromatic volatile organic compounds (VOCs), such as toluene, benzene, chlorobenzene, *p*-xylene or mesitylene, produces a reversible blue-shift in the emission. It is noted that the *trans* isomer does not exhibit vapochromic behaviour, which is attributed to its less open structure, with shorter metal–metal distances, and an efficient π–π stacking of isocyanide ligands [86]. Rod-like crystals over 500 μm in length have been obtained for the analogue *cis*-[Pt(CN^{t}Bu)$_2$(CN)$_2$] using an injection–reprecipitation method. These Pt^{II}–Pt^{II} stacked ‘wires’ exhibit intense green emission which shifts significantly, and/or increases in intensity, on exposure to VOCs [87]. [Pt(CN)$_2$(4,4′-dicarboxy-2,2′-bpy)] forms several intensely coloured polymorphs depending on pH and crystallization solvents. Interconversion between the various polymorphs occurs in solution and also on exposure of the crystals to different solvent vapours. It is suggested that bulky substituents on the bipyridine ligand favour the formation of cavities in the crystal lattices and the subsequent inclusion of guests [88]. The red potassium salt [K(H$_2$O)][Pt(bzq)(CN)$_2$] (bzq is 7,8-benzoquinolinato) has been used to prepare vapochromic films that become yellow in the presence of solvent vapours, such as dichloromethane, methanol, ethanol, acetone, tetrahydrofuran, or acetonitrile, after exposure times ranging from 5 s (methanol) to 45 min (tetrahydrofuran) [89]. In other examples, Pt–Pt interactions are not directly involved in the vapochromic behaviour of the complexes [90, 91]. For example, crystals of the intensely luminescent solvated complex **10a** $6CHCl_3 \cdot C_5H_{12}$ (Fig. 10) change colour on desolvation and show a significant decrease in emission intensity [91]. The original colour and intense emission are restored upon exposition to the vapour of halogenated solvents or small polar VOCs (e.g. THF, acetone, or diethyl ether), but not to aromatics, methanol or ethanol. It has been shown that the solvated structure contains voids or solvent channels with an extended network of CH–π and π–π interactions, which rearrange on desolvation, giving a more compact packing, and presumably favouring quenching of the luminescence via inter-molecular dipole–dipole interactions. The incorporation of halogenated and small polar solvents is favoured by the formation of relatively strong CH–π, π–π, CH–X and X–X interactions, whereas the size of the voids may be too small to host aromatic VOCs. In the case of derivatives **10b** and **10c** (Fig. 10) [90] the alkynyl moieties act as convenient receptors for chlorinated solvents via multiple CH–π(C≡C) interactions.

Since the early example of Balch et al. [92] of solvent-induced luminescence of a trigold(I) complex, attributed to the presence of columnar Au^I–Au^I interactions, other examples have been proposed as efficient VOC detectors based on extended metal–metal contacts involving Au(I), as well as other d^{10} metal ions. For example, Fernandez et al. described the vapochromic and vapoluminescent behaviour of $\{Tl[Au(C_6Cl_5)_2]\}_n$ (**10d**, Fig. 10), which exhibits a 3D network of Au^I–Tl^I interactions

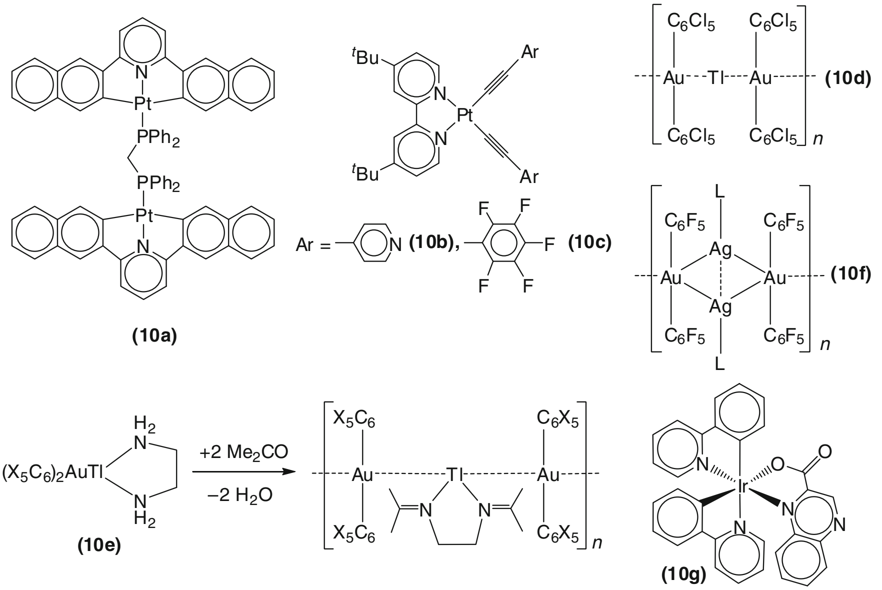

Fig. 10 Examples of vapochromic/vapoluminescent metal complexes

with channels into which the VOCs can diffuse [93, 94]. Reversible changes of colour are observed when the solid is exposed to a variety of VOCs, such as acetone, acetonitrile, triethylamine, acetylacetone, tetrahydrothiophene, 2-fluoropyridine, tetrahydrofuran, and pyridine vapours. The luminescence of **10d** has its origin largely in the Au^I–Tl^I contacts, and binding of the Tl atoms to the VOCs are believed to be responsible for the observed behaviour. Interestingly, the colour change observed when $[(X_5C_6)_2AuTl(ethylenediamine)]_n$ (X is Cl, F; **10e**) reacts with ketone vapours in the solid-state is associated to condensation reactions at the amine moieties, promoted by their coordination to Tl (Fig. 10) [95]. Polymeric Au^I/Ag^I complexes $\{Ag_2L_2[Au(C_6F_5)_2]_2\}_n$ (L is Et_2O, Me_2CO, THF, CH_3CN; **10f**, Fig. 10) also show fast vapochromic and vapoluminescent behaviour towards a variety of VOCs. Recent studies have proven that substitution reactions between the ligand at the Ag atoms and the VOCs are responsible for the observed behaviour, and that the emission is localized in the tetranuclear Au^I/Ag^I cores [96]. This type of Au^I/Ag^I polymers can be incorporated into fibre optics for optical measurements [97–102]. The coordination polymers $\{Cu[Au(CN)_2](solvent)_2\}_n$, which can be obtained in two polymorphic forms depending on the solvent, exhibit visible colour changes on exposure to various volatiles, including water, MeCN, DMF, dioxane, pyridine and NH_3. This is due to their coordination to the Cu(II) centres, each analyte modifying the crystal field splitting differently [103]. A related compound, $\{Zn[Au(CN)_2]\}_n$, responds to NH_3 with detection limits as low as 1 ppb [104].

The Ir(III) cyclometallated complex **10g** (Fig. 10) shows selective vapochromic and vapoluminescent properties in response to acetonitrile or propiononitrile vapour, while remaining unchanged for other VOCs [105]. Crystals of the compound change from a black to a red polymorph in less than 1 min on exposure to the solvent vapours; at the same time, strong emission is switched ‘on’ (red form). Structural analyses show that the black form exhibits shorter π–π stacking distances between the quinoxaline ligands of neighbouring molecules, which favours dipole–dipole interactions and quenching of the luminescence.

4.2 Detection of Small Organic Molecules in Solution

The detection of small organic species in solution has proven to be a significant challenge, and has received surprisingly little attention. The *fac*-carbonyl Re molecular squares, bearing organometallic fragments, have featured in a number of studies, building on their observed recognition of both anionic and volatile organic species [52]. The large Re(I) cornered square bridged by zinc porphyrin moieties **11a** (Fig. 11), demonstrate considerable red shifts in the porphyrin based fluorescence on the addition of millimolar quantities of pyridine, but not with toluene [106]. In the simple neutral cyclophanes **11b**–**11d** (Fig. 11), which posses a variety of different rigid spacers, the luminescence quenching rate constants, k_q, of the ^{3}MLCT excited state have been investigated in the presence of a variety of

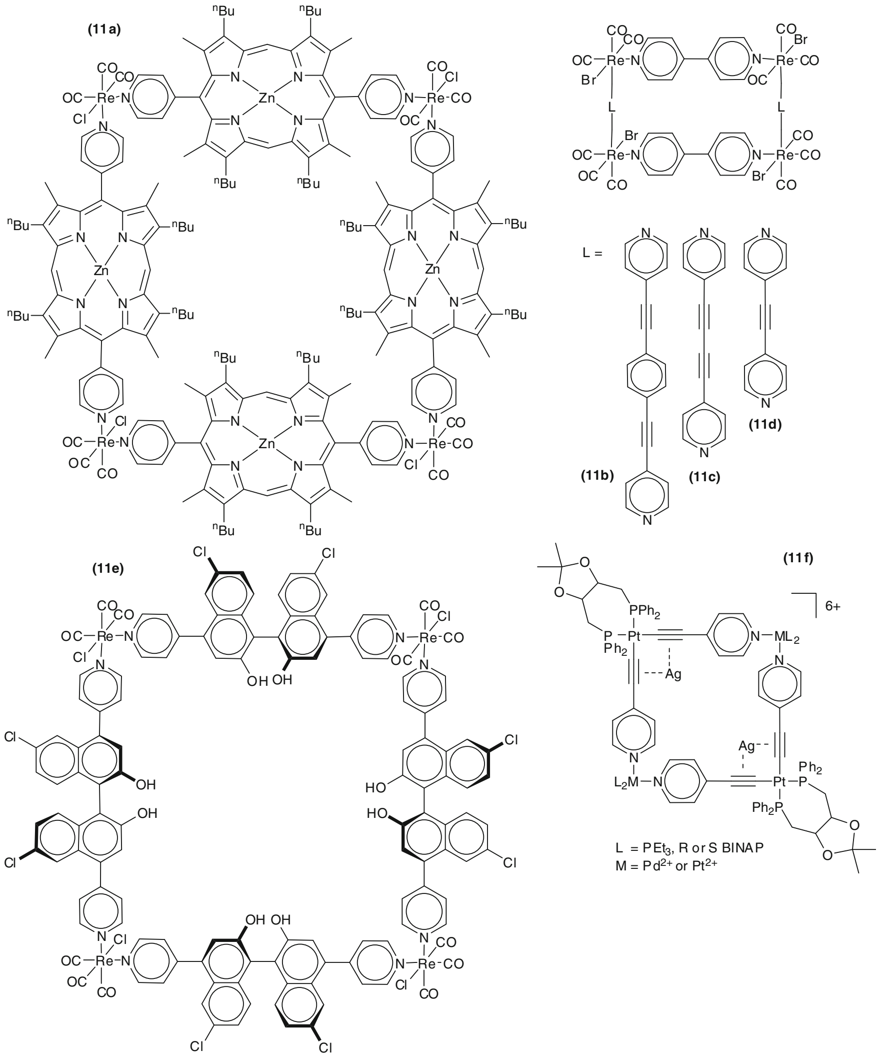

Fig. 11 Examples of optical detectors for small molecules

aromatic amines such aniline and were found to be higher than those for simple monomeric Re(I) complexes [107]. In another example an enantiopure square **11e** (Fig. 11) undergoes luminescence quenching with the chiral alcohol, *R*- or *S*-2-amino-1-propanol, and in the process demonstrates an enantioselectivity of 1.22, determined by differential quenching rates [108]. The optically active mixed, neutral Pt/Pt/Ag and Pt/Pd/Ag macrocyclic complexes (**11f**; Fig. 11) have undergone an exploration for the inclusion of several diamines demonstrating a significant interaction with the neutral guests tetramethylpyrazine and phenazine, detected by perturbations in the circular dichroism spectra [109].

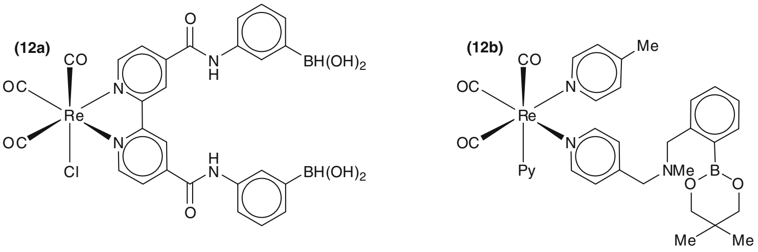

Fig. 12 Examples of Re(I) complexes for the optical detection of glucose

The detection of sugar has attracted a number of studies. The neutral diboronic acid complex **12a** (Fig. 12) was reported by Yam et al., illustrating a preference for mono-saccharides and a marginal preference for D-fructose ($pK_s = 2.40$ in DMSO), through a perturbation in the ^{3}MLCT transition, and an increase in the observed emission [110]. There is, however, considerable complexity to the system in aqueous solution given the pH dependence of the boronic acid groups [111]. Glucose testing with a structurally similar complex **12b** (Fig. 12) showed a significant dependence on the solvent system used; in methanol, a 55% fluorescence intensity increase was observed with a change in glucose concentration from 0 to 400 mg dL^{-1}, although in a methanol-phosphate buffered saline solution, no significant response was found to glucose at physiological pH [112].

A competitive indicator displacement approach has been successfully employed for sulfhydryl amino acids and short chain peptides using heterobimetallic donor–acceptor complexes: *cis*-$[ML_2(\mu\text{-}CN)_2\{Pt(DMSO)Cl_2\}_2]$ (M is Fe^{2+}, Ru^{2+} and Os^{2+} and L is 2,2′-bpy). The *cis*-$[ML_2(CN)_2]$ units are used as signalling indicators, and $\{Pt(DMSO)Cl_2\}$ as both an acceptor group, and the receptor for the analytes. All three ensembles are able to produce specific colorimetric/fluorometric responses to cysteine, homocysteine and methionine, as well as the sulfhydryl-containing small peptide glutathione [113, 114]. In a very recent paper, an alternative strategy, employing an Ir(III) complex $[Ir(pba)_2(acac)]$ (Hpba is 4-(2-pyridyl)benzaldehyde and acac is acetylacetone) has been shown to posses selectivity for homocysteine. Upon addition of the amino acid, in a semi-aqueous solution, a colour change from orange to yellow and a luminescent variation from deep red to green were evident to the naked eye, attributed to the formation of a thiazinane group from the free aldehyde group [115].

5 Sensing of Large Biomolecules

5.1 Detection of DNA

The development of probes for large biomolecules has attracted considerable attention using luminescent late transition metals, particularly Ru(II) polypyridyl

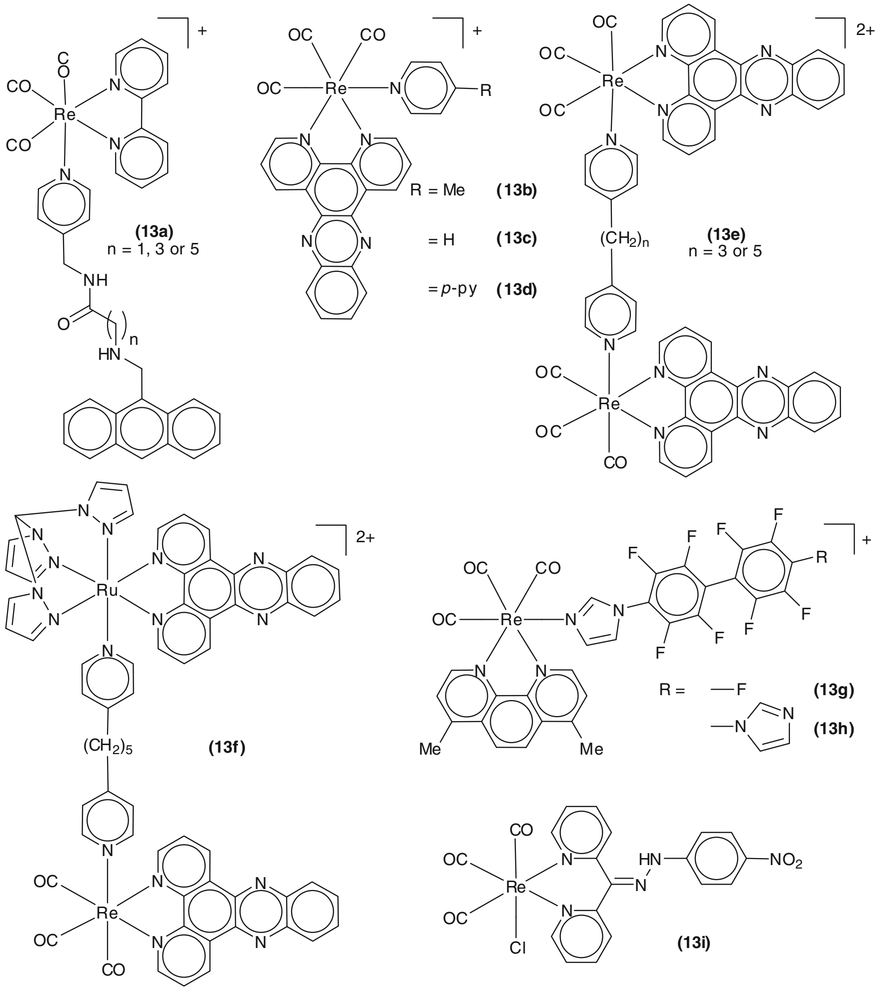

Fig. 13 Examples of Re(I) complexes for the optical detection of biomolecules

lumophores. Attention has been given to sensing the presence of DNA, and has been the subject of several review articles [116–118]. As with other areas of molecular detection, the fluorescent Re(I) moiety has been the subject of a number of studies. Schanze and Thornton isolated a series of complexes (**13a**, Fig. 13), structurally related to the anion recognition unit to **6j** (Fig. 6), bearing an anthracene unit [119, 120]. The complexes exhibit dual emission from both the metal ^{3}MLCT and the anthracene unit, although significant quenching is observed. On addition of DNA, hypsochromism of the anthracene absorption is detected, but not in the Re centred transitions, suggesting that the planar anthracene group is intercalating in the DNA. A dramatic increase was observed in the ^{3}MLCT emission in keeping with many transition based metal complexes associated with the hydrophobic DNA environment. Building on these results, a similar 'light-switch' interaction was observed with the Re(I) complex **13b** (Fig. 13), bearing the intercalating ligand dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz). In aqueous solution the complex is non-luminescent, whereas $^3IL_{dppz}$ phosphorescence is observed from the aqueous DNA bound complex [121]. Similar behaviour was observed with two structurally related complexes (**13c** and **13d**, Fig. 13), which exhibited potential for photo-cleavage of DNA [122, 123]. Recent developments include the consideration of bimetallic complexes, such as **13e**, where a hypsochromic shift in both the MLCT and IL transitions when added to buffered DNA [124]. Studies with the hetero-dinuclear complex **13f** reveal energy transfer between the Re(I) and the Ru(II) centres, and a light-switch behaviour in the emission on the introduction of DNA [125].

5.2 Detection of Proteins

The use of fluorescent organometallic complexes to label biological substrates is beginning to provide some exciting alternatives to the more traditional organic dyes [126], with suitable iridium [127–129], rhodium [130], platinum [131], rhenium [132–135] and osmium [136] examples having recently been reported. The Re diimine 'wires' (**13g** and **13h**, Fig. 13), have been shown to form complexes with the nitric oxide synthase mutant δ114 [137]. Steady-state luminescence measurements with **13h** establish a dissociation constant of 100 nM, while **13h** binds with a K_d of 5 μM, causing partial displacement of water from the haeme iron. The optical behaviour of (**13i**, Fig. 13), in the presence of L-methionine, and chemotactic *N*-formyl-amino acids: *N*-formyl-L-methionine, *N*-formyl-L-glycine and *N*-formyl-L-phenylalanine shows the complex to be insensitive to L-methionine, but highly sensitive to the *N*-formylamino acids at concentrations of less than 10^{-5} M in non-aqueous polar solvents, and is dependant on the polarity of the side chain of the amino acids.

Considerable progress has been made by the group of Lo in developing organometallic probes capable of recognizing the presence of specific classes of proteins, and has recently been the subject of a detailed review [138]. To highlight some recent advances, a large number of *fac*-carbonyl Re(I) (**14a**–**14c**, Fig. 14) [139–141] and cyclometallated Ir(III) complexes (**15a**–**15c**, Fig. 15) [142–144] bearing biotin moieties have been reported. Each of these complexes exhibit the characteristic ^3MLCT emission in solution, which was significantly enhanced in the presence of the glycoprotein avidin. Furthermore, the inclusion of the extended planar ligands dppz and dppn has been shown to permit similar enhancement to be observed in the presence of DNA [141, 145].

In another exciting development, the inclusion of a thiocyanate group into the ligands of complex **14b** has allowed the complex not only to bind to avidin, but also to be tagged to bovine serum albumin (BSA) [146]. The inclusion of indole groups

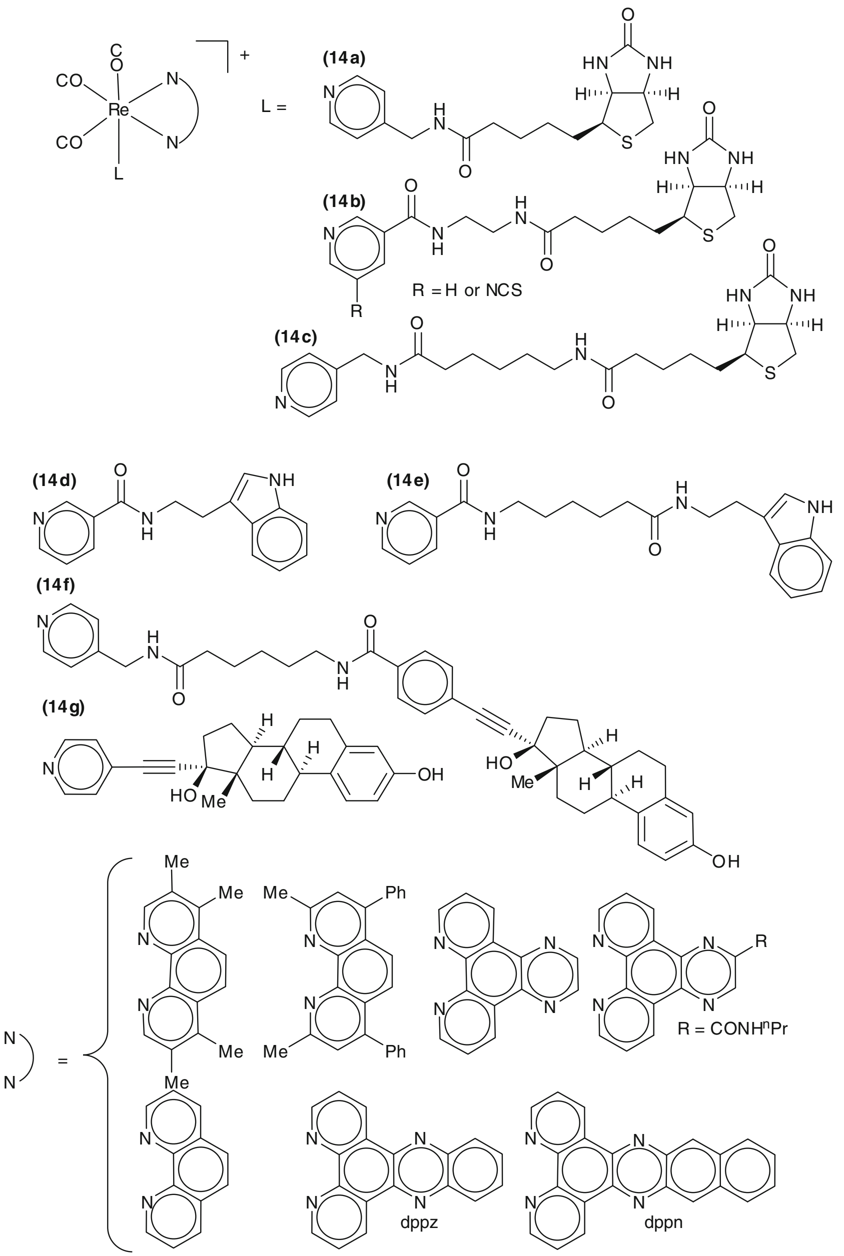

Fig. 14 Examples of Re(I) complexes used in the optical detection of biomolecules

into both the Re(I) (**14d** and **14e**, Fig. 14) chromophores [147, 148] show enhanced emission in the presence of indole binding proteins including BSA and tryptophanase, despite having excellent emission in aqueous solution. Similarly, the estrodiol

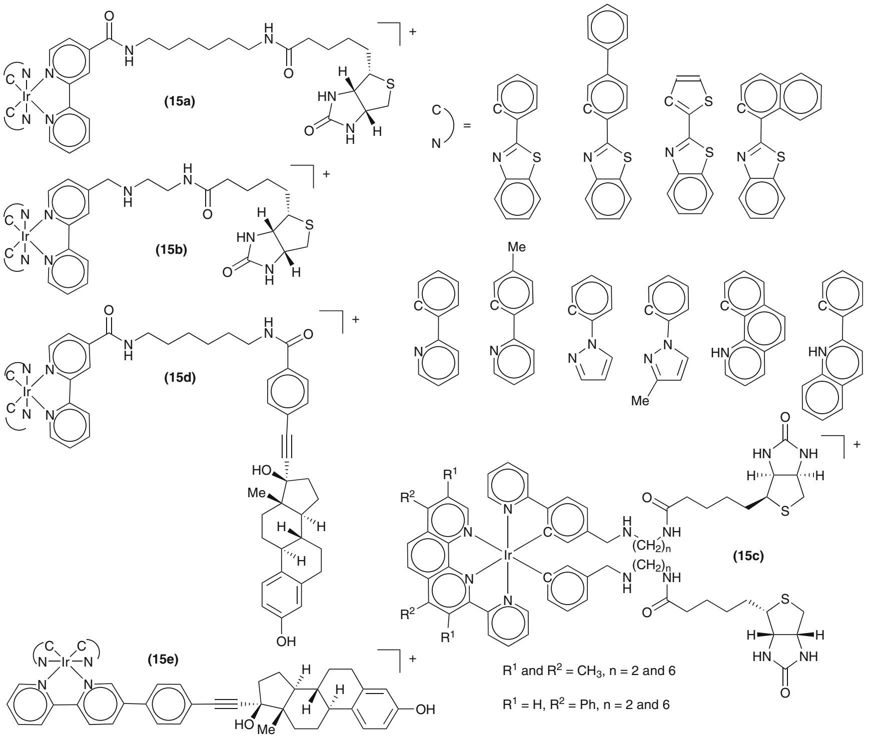

Fig. 15 Examples of Ir(III) complexes for the optical detection of protein interactions

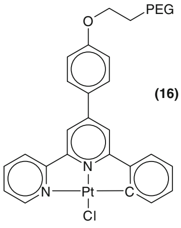

Fig. 16 An example of a Pt(II) complex with sensing properties for protein surfaces

containing Re(I) complexes (**14f** and **14g**, Fig. 14) [149] and the related Ir(III) complexes (**15d** and **15e**, Fig. 15) [150], demonstrate lifetime extension and enhanced fluorescence in the presence of oestrogen receptor α. In a related study, a cyclometallated Pt(II) complex (**16**, Fig. 16), bearing an extended poly(ethylene glycol) has demonstrated that the photoluminescence is enhanced in the presence of the hydrophobic regions of proteins such as BSA in aqueous solution [151].

6 Conclusions and Outlook

The versatility of organometallic complexes in optical sensing has been demonstrated by the variety of sensor compounds developed in recent years and the wide range of analytes that have been targeted. New research has built upon the properties of well-known chromophores, such as Re(I), Ir(III) or Ru(II) complexes, but also on less common species, such as Au–Tl/Ag networks or metal-containing self-assembled macrocycles, and has produced sophisticated architectures able of dual responses (e.g. optical and electrochemical) or containing various recognition sites appropriate for logic gates. Detailed systematic studies on the optical and structural properties of the complexes before and after inclusion of the analytes has brought a much better understanding of the mechanisms involved in the molecular recognition and reporting events. This fundamental research is essential to improve and predict the selectivity and sensitivity of the sensors, and further work is still needed if a rational design of sensors for specific target analytes is to be achieved. A further challenge will be the development of sensing devices with commercial potential. Whereas some examples of the incorporation of organometallic sensors into working optical devices have been reported, these are still scarce. However, given the increasing interest for reliable and cost-effective sensors for environmental and medical applications, this area is likely to receive much attention in coming years.

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