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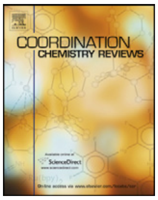

Review

Sensory luminescent iridium(III) and platinum(II) complexes for cation recognition

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ABSTRACT

This article presents the design and photophysical properties of platinum and iridium complexes incorporating a host receptor for metal cations, with particular attention to the changes in their luminescence properties upon addition of these ions in solution. Selected examples on cationic and neutral complexes within the families of Pt and Ir complexes will be presented. A series of platinum acetylide complexes incorporating a crown ether unit have been designed and prepared for the detection of alkali and alkaline-earth cations. Similarly, Ir complexes, cationic and neutral species, have been used as luminophores using the same receptor units. Metal-based chemosensors for transition- and heavy-metal ions have been also developed. The detection of divalent metal cations such as Zn^{2+}, Cd^{2+} and Cu^{2+}, has been achieved thanks to the interesting chelating properties of di(2-picolyl)amine (2,2′-DPA) ionophore. Introducing appropriate substituents (flavone, macrocyclic pyridine) on the ancillary acetylide ligand of cyclometalated platinum(II) allows the recognition of Pb^{2+} ions. Mercury(II), a thiophilic metal ion, interacts with the sulfur atom of cyclometalated ligands of iridium complexes inducing remarkable emission spectral changes. These luminescent metal-based sensors give rise to phosphorescence turn-on or turn-off effects as well as changes in the emission wavelength and/or emission lifetime.

1. Introduction

The development of sensory systems displaying rapid real-time response to chemical and biological analytes continues to lie at the forefront of fundamental research. Among chemosensors, light-active probes incorporating host receptors have served as reporter systems for metal ion binding. In this context, extensive work has been devoted to transition metal based luminescent systems capable of the detection of environmental changes [1–4], because of their advantages such as significant Stoke shifts allowing easy separation of excitation and emission, long emissive lifetimes compared to those of purely organic luminophores and large emission shifts from changes in the local environment compared with those

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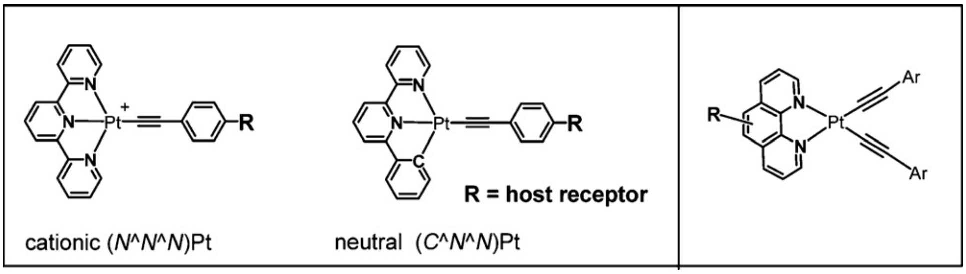


Chart 1. Platinum(II) organometallic complexes used as phosphorescent chromophores.

of organic emitters. Among them, phosphorescent square-planar d^8 Pt(II) [5] and octahedral d^6 Ir(III) [6] complexes are the most promising candidates because of their thermal stability and rich photophysical properties. The charge-transfer absorption bands and the luminescence properties of these series of complexes can be fine-tuned by structural modification of the ligands, so that they are perfectly adapted to chemosensing. In addition, due to the strong spin-orbit interaction, the incorporation of heavy metal atom increases the intersystem-crossing rates and thus the efficiency of phosphorescence. Polyimine Pt(II) and Ir(III) complexes are particularly promising candidates for advanced applications including vapochromic [7–10], vapoluminescent [8,12] and solution-based luminescent sensors, [10–21] biomedical probes and medicinal chemistry [18,22–25].

The scope of this article is confined to the ion binding properties of metal complexes (Pt, Ir) containing host receptor(s) R onto their ligands, where R denotes a receptor for metal cations, and their optical responses, with particular attention to the changes in their luminescence properties upon addition of these ions in solution. Selected examples on cationic and neutral complexes within the families of Pt and Ir complexes will be presented, as depicted in Charts 1 and 2. A series of platinum acetylide complexes incorporating a host receptor R have been designed and prepared, the host receptor being introduced onto either diverse polyimine ligands or the arylacetylide ligand. Similarly, Ir complexes, cationic and neutral species, were used as luminophores using the same receptor units.

Beside the choice of the metal-based chromophore, the rational design of luminescent sensors involves the choice of the nature and the location of the receptor R. Although the signaling mechanism is not always predictable, the position of R onto the complex is also of importance. The optical response for metal ion binding is based on the interchange between two different excited states. The signaling mechanisms leading to *switch on/off* systems generally involve photoinduced electron/energy transfer (PET). Other processes are operative: the complexation with analytes can change the lowest excited state of the complexes, inducing a change in both the absorption and the emission properties of complexes, as it is in a switch from ligand-to-ligand charge transfer (LLCT) or intramolecular charge transfer (ILCT) to emissive metal-ligand charge transfer (MLCT). Up to date, we are not aware of mechanisms involving of excimer/exciplex, excited-state intra/intermolecular proton transfer (ESIPT), processes for metal complexes whereas numerous examples have been published for fluorescent probes [26].

This article will be divided into three parts, the first one will be devoted to metal complexes (Pt, Ir) incorporating crown-ether units, the second to dipicolylamino (DPA)-based metal systems and the third one to lead(II) and mercury(II) ions chemosensors. General surveys dealing with the use of heavy metal complexes for sensing have already been published early on and continuously reviewed during the past few years. For insance, Lo et al. have described the design of luminescent rhenium(I) and iridium(III) polypyridine complexes as probes for ions, small molecules and biomolecules such as DNA and proteins. [19] In addition, recent developments of phosphorescent chemosensors based on heavy-metal complexes (Pt(II), Ru(II), Re(II), Ir(III), Cu(I), Au(I)) recently appeared [20,21], These articles demonstrate the impact of metal-based systems for sensing and their applications in bio-imaging. Herein, we will point out the crucial importance of the design of ligands incorporating recognition units for metal cations. We will emphasize on the design of cyclometalated platinum(II) and iridium(III) complexes as a way to significantly influence the optical response to a recognition event. In particular, the use of flavone and macrocyclic pyridine as receptors, which has not been reviewed so far, will be described.

These luminescent metal-based sensors give rise to *switch on/off* or *ratiometric* mechanism processes. Luminescent sensors, in which a luminophore is linked to a host receptor unit, frequently utilize the ion binding to supress intramolecular electron transfer which quenches the luminescence of the metal ion free chromophore. This is generally the case of azacrown ether-based sensors in which an electron transfer is intramolecularly transferred to the emitting MLCT state, leading to a quenching. Binding of the analyte to the lone pair of nitrogen atom restores the MLCT emission. According to this concept, several Pt and Ir complexes have been synthesized. The same mechanism process is operative for the dipicolylamine (DPA)-based systems, for which the binding properties leading to an optical response relies on the amino group. A change of the nature of the emitting state upon metal cation

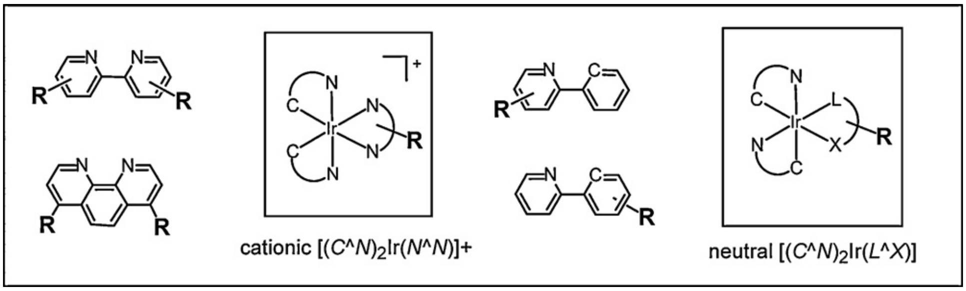
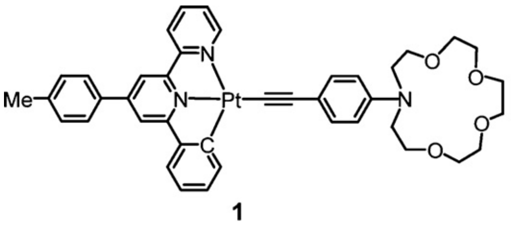


Chart 2. Iridium(III) organometallic complexes used as phosphorescent chromophores.



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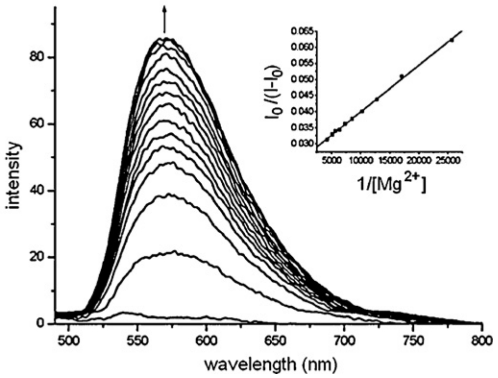


Fig. 1. Luminescence spectra of 1 (1.2×10^{-5} M) in MeCN in the presence of Mg^{2+}. The inset shows the plot of $I_0/(I - I_0)$ vs $[Mg^{2+}]^{-1}$. $\lambda_{exc} = 465$ nm. This figure was reproduced from Ref. [29] with permission of the copyright holders.

chelation leading to *ratiometric* mechanism processes, will be also described. More interestingly, the peculiar behavior upon metal-binding cation are observed in the case of flavone- or macrocyclic pyridine-based complexes, a change of phosphorescence to fluorescence or a switch of charge transfer to another direction will be presented.

2. Crown-ether containing transition metal (Pt, Ir) complex systems: luminescent sensors for alkali metal and alkaline-earth metal ions

2.1. Platinum(II) complexes

One successful strategy used to construct long-lived and emissive d^8 square–planar Pt(II) complexes for metal ion recognition involves functionalization of the ancillary acetylide ligand [27,28]. Several (*CN̂N̂*-phenylbipyridine) and (*NN̂N̂*-terpyridine)Pt complexes have been described for the detection of alkali metal and alkaline-earth metal cations such as Na^+, K^+, Ca^{2+}, Mg^{2+} and Ba^{2+}. One example of a functionalized (*NN̂N̂*-R-phenanthroline)Pt(bis-acetylide) complex was also reported.

2.1.1. Neutral (C^N^N-phenylbipyridine)Pt complexes

The ion binding properties of the cyclometalated *(CN̂N̂-phenylbipyridine)platinum(II) acetylide* complex **1** containing the N-phenylaza-15-crown-5 moiety in the acetylide ligand has been reported [29]. Substantial luminescence enhancement ($\lambda_{em} = 570$ nm) was observed upon addition of Mg^{2+} to an acetonitrile solution of complex **1**. In the absence of cations, complex **1** is non-emissive due to rapid internal conversion from the ^{3}MLCT to the ^{3}LLCT state and facile non-radiative deactivation of the low-lying ^{3}LLCT state. Upon complexation of Mg^{2+} ions (1:1 ratio), bright luminescence is observed (Fig. 1), as the result of a decrease of the electron-donating ability of the acetylide ligand. The emission enhancement in 1-Mg^{2+} has been attributed to a shift of the non-emissive ^{3}LLCT to higher energies, resulting in the ^{3}MLCT emissive state being the lowest-lying excited state. This behavior contrasts with that of the related cationic terpyridine complex **3**, featuring the same metal ion receptor on the acetylide ligand, for which no luminescence enhancement was observed upon cation binding (see below).

In contrast, Li^+, Na^+, K^+, Ca^{2+} and Ba^{2+} do not cause the change of luminescence of **1**, despite complexation of these ions within the azacrown cavity as reflected by absorption changes. To account for these observations, the kinetic model of Schanze is proposed [30]. M^{n+} ions can be released from the azacrown unit during the lifetime of the MLCT state, since Pt(III) leads to a decrease of the charge density on the amino group in MLCT state (Scheme 1).

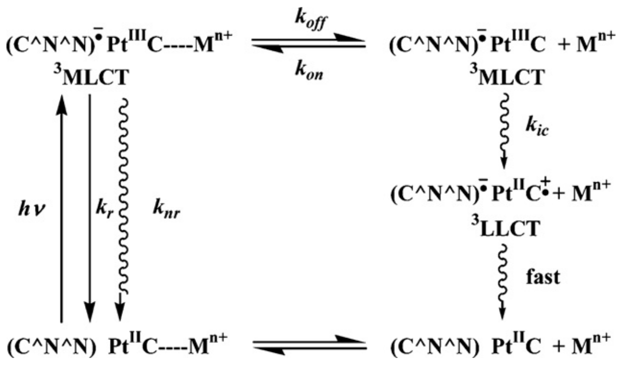
2.1.2. Cationic (N^N^N-terpyridine)Pt complexes

Aiming at exploring the optical responses of *platinum(II) terpyridine* moieties toward cations, Yam et al. [31,32] studied the differences in the cation-binding ability between the two terpyridine complexes **2** and **3** in their *triflate salts* with metal ions such as Na^+, Li^+, Mg^{2+}, Ca^{2+}, Cd^{2+} and Zn^{2+} in acetonitrile (Scheme 2).

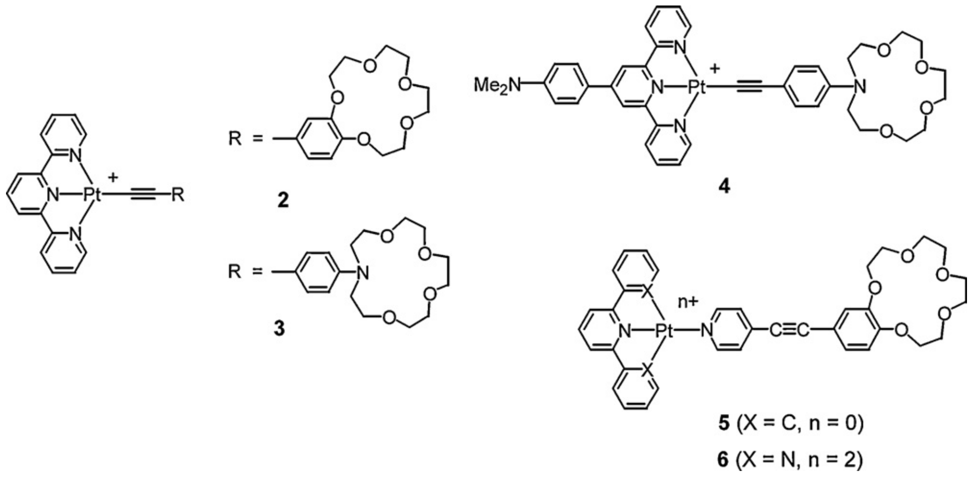
Upon addition of Ca^{2+} or Mg^{2+} ions to an acetonitrile solution of complex **2**, significant luminescence enhancements of more than 31-fold and 8-fold were observed. Similar studies with complex **3** that contains an azacrown ether moiety were also pursued with the same set of metal ions. Different spectral absorption changes were observed for mono- and divalent metal ion complexation with **3**, but importantly, no significant luminescence enhancement was observed.

Complexes **2** and **3** are non-emissive in acetonitrile solution at room temperature. This was attributed to the intramolecular photoinduced electron transfer (PET), in which the electron is transferred from the electron-rich donor substituent group on the alkynyl ligand to the platinum metal center to quench the emissive ^{3}MLCT excited state. This *switching on* of luminescence upon metal ion-binding was attributed to the blocking of the photoinduced electron transfer quenching mechanism, since coordination of metal ions into the crown cavity would remove the ability of the donor atoms on the crown unit to quench the emissive ^{3}MLCT state by intramolecular reductive electron transfer.

In another report, similar studies have been performed on 3 as ClO_4^- salt: the lack of emission for the cation-bound **3** (Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}) was attributed to the dissociation of the crowned cation from the azacrown within the lifetime of the ^{3}MLCT state, and the rapid internal conversion from the ^{3}MLCT to the ^{3}LLCT states for the cation-free complex, as depicted in Scheme 1 [33].



Scheme 1.



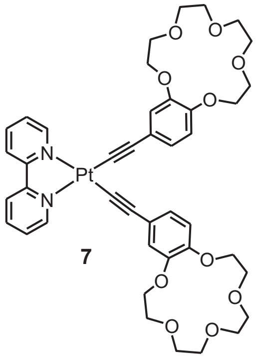
Scheme 2. Molecular structures of platinum(II) complexes with crown-ether pendants.

The spectral changes of complex **3** as PF_6^- salts upon addition of guest metal (in MeCN) was monitored by electronic absorption studies [34]. For Na^+, a 1:1 binding mode with log K 1.40 (±0.01) was observed while for K^+ both complexes with stochiometries 1:1 and 2:1 were formed with K_{11} 1.99 (±0.05) and K_{21} 2.79 (±0.05), respectively. The ion-binding properties have been confirmed by positive ESI mass spectrometry.

Related studies have been performed by using absorption spectroscopies. The azacrown ether in complex **4** (Scheme 2) is capable of complexing metal cations (Ca^{2+}, Ba^{2+}, Mg^{2+}, Sr^{2+}) resulting in an excited state switching from LLCT to ILCT. The ILCT transition from the phenyl π orbitals to the π^* orbitals of the terpyridyl moiety becomes the lowest-energy excited state [35].

In the other hand, the cation-binding properties of the crown-ether containing complexes **5** and **6** have been studied (Scheme 2). The spectral changes upon addition of guest metal ions were monitored by electronic absorption and ^1H NMR studies. Complex **5** has larger binding constants than its terpyridyl analogue complex **6**. This is attributed to the absence of charge in complex **5** which could give rise to stronger binding affinities for metal ions [36].

Bis-acetylide Pt complexes have been also investigated, the crown ether receptor(s) could be attached to either the diimine or the acetylide ligands [37,38]. It is noteworthy that complex **8** is the only example of an acetylide complex in which the crown-ether is attached to the diimine ligand. In both cases, modification of the luminescence spectra were observed upon addition of Ca^{2+} [38]. The design of **8** is of interest since complexation of metal cations is expected to be favored, since the LUMO is mainly localized on the diimine ligand acting as π^* acceptor.



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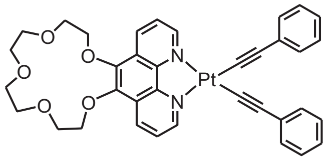

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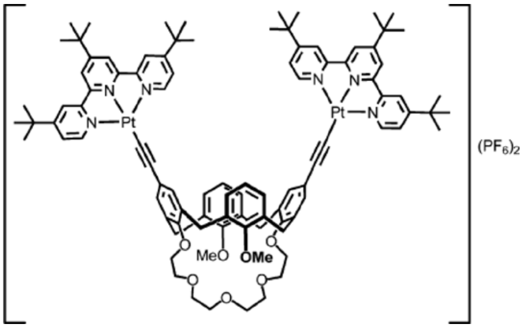
2.1.3. Dinuclear (terpyridine)Pt complexes with a calix[4]crown-5 alkynyl ligand

A dinuclear platinum(II) alkynylcalix[4]crown-5 complex shows luminescence enhancement upon metal ion-binding, with a more selective binding toward K^+ over the other alkali metal and alkaline-earth metal ions [39].



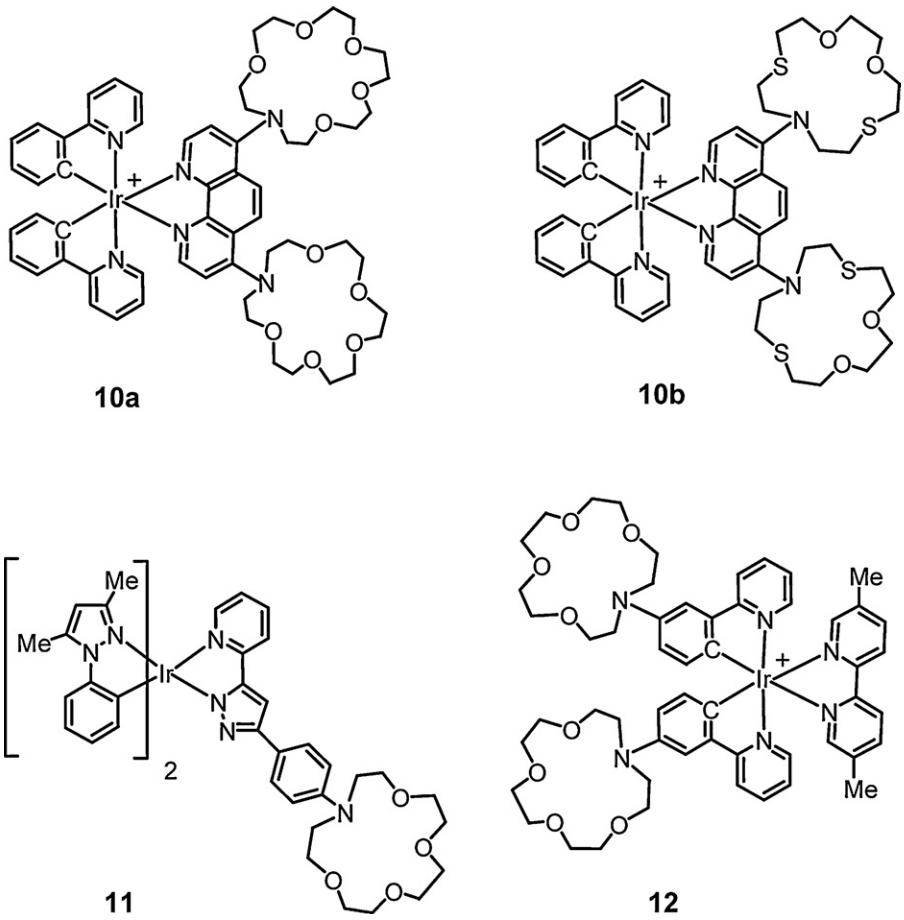
Upon excitation at $\lambda \geq 400$ nm, complex **9** displayed a weak emission band in acetonitrile solution at 738 nm. This weakly emissive behavior can probably be attributed to a photoinduced electron transfer (PET) process, in which the electron is transferred from the electron-rich alkoxysubstituted calixcrown moiety to the platinum terpyridyl unit that quenched the emissive ^{3}MLCT excited state.

The changes in the luminescence response of **9** toward Li^+, Na^+, and K^+ ions were studied. The emission spectra showed a blue shift in energy to ca. 635–685 nm upon inclusion of the respective Li^+, Na^+, and K^+ ions, with a concomitant substantial enhancement of the emission intensities. The platinum(II) calixcrown complex exhibits stronger luminescence enhancement in the presence of K^+ ions, with selectivities 100-fold greater than those for Na^+, Li^+, and Cs^+ and alkaline-earth metal ions such as Mg^{2+} and Ca^{2+}. The improved selectivity in this system compared to that in other related platinum(II) terpyridyl systems with crown ether pendants is ascribed to the pre-organized conformation of the calixcrown with high rigidity over the crown ether unit.

2.2. Iridium (III) complexes

Azacrown receptor(s), and its derivatives have been also incorporated onto luminescent Ir complexes, using a phenanthroline, a pyridylpyrazolate or phenylpyridine ligands (Scheme 3).

The two azacrown ether appended Ir complexes **10a** and **10b** have been described as probes for metal cations by using pho-



Scheme 3. Molecular structures of iridium(III) with crown ether pendants.

toluminescence and electrochemiluminescence (ECL). [40,41] In addition, Ir complexes containing azacrown ethers as host receptors show stronger emission increase in presence of metal ions than the analogous ruthenium probes [42].

Upon addition of Ba^{2+}, complex **10a** exhibited an ~8-fold enhancement of the intensity of the emission, along with a red shift (Fig. 2). The aza-dithia-dioxa crown-ether appended iridium complex **10b** exhibited selective binding properties toward Ag^+ and Hg^{2+} ions in aqueous media by characteristic luminescence response. In the presence of Ag^+, the emission intensity of 10b was enhanced ~3.4 fold and was accompanied by a pronounced red-shift (Fig. 3). These results can be rationalized by a change of the emission from ^{3}LC to ^{3}MLCT, because the metal ion binding phenanthroline ligand becomes a better acceptor. In contrast, the addition of Hg^{2+} quenched the emission (~80%) of **10b**, equally showing a λ_{em} red-shift. The binding modes and association constants were determined (one step association **10b•**$(Ag^+)_2$, $K(Ag^+) = 8.6 \pm 0.1$; **10b•**$(Hg^{2+})_2$, $K(Hg^{2+}) = 9.0 \pm 0.1$). ^{1}H NMR titration and ESI-MS experiments support the 2:1 binding model.

ECL responses of the above two complexes were also assessed. Complexes **10a** and **10b** exhibit a noticeable ECL sensing for Ba^{2+} and Ag^+ in MeCN with tri *n*-propylamine as co-reactant, respectively. Complex **10a** showed a gradual enhancement of ECL emission and a concomitant λ_{em}ECL red shift. The LUMO resides predominantly on the azacrown ether phenanthroline ligand which is responsible for the metal uptake. This design allows the metal cations to remain coordinated in the emitting states.

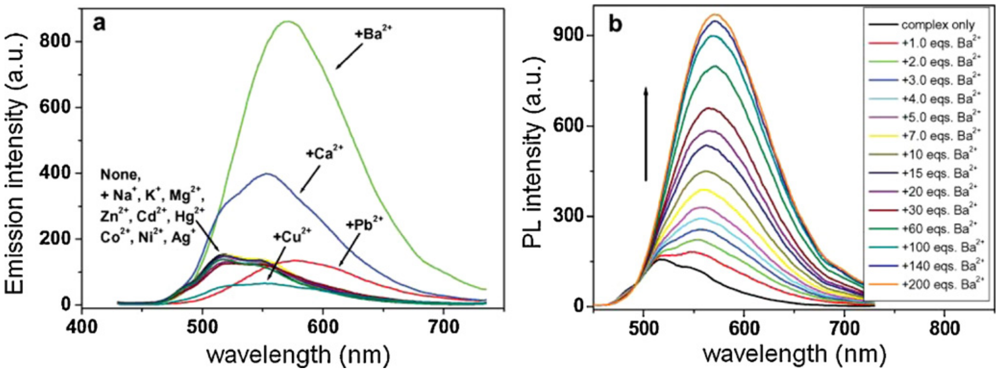


Fig. 2. (a) PL responses of **10a** (10 mM inMeCN) with increasing concentrations of Ba^{2+} (λ_{exc} = 374 nm) (b) PL (λ_{exc} = 374 nm) responses of **10a** (10 mM) in MeCN upon addition of 100 equiv. of metal ions. This figure was reproduced from Ref. [41] with permission of the copyright holders.

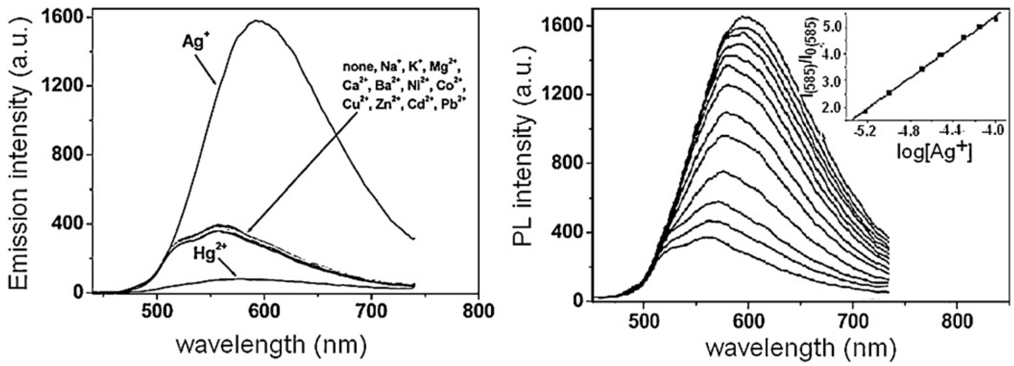


Fig. 3. (Left) Effects on the emission of 10b (5.0 μM in MeCN/H_2O = 1:1) upon addition of different metal ions (100 equiv). The excitation wavelength was set to 375 nm. (Right) Emission intensity responses of **10b** (5.0 μM in MeCN/H_2O = 1:1) upon addition of 3.0, 6.0, 10, 20, 30, 70, 100, 150, 200, 300, and 500 μM Ag^+ ions. Inset: The correlation between emission intensity of **10b** at 595 nm and log [Ag^+]. The excitation wavelength was 375 nm. This figure was reproduced from Ref. [40] with permission of the copyright holders.

The attachment of the azacrown fragment to an anionic pyridylpyrazolate ligand leads to a neutral Ir(III) complex **11** (Scheme 3) [43]. Such a neutral-charge complex is expected to provide a better sensitivity in recognizing metal cations. For example, drastic changes on the Ca^{2+} phosphorescence titration were observed: the 560 nm phosphorescence was gradually blue-shifted toward 520 nm, accompanied by the increase of the emission intensity. Titration gave a two-species equilibrium, consistent with a 1: 1 (11: Ca^{2+}) binding mode. Based on DFT calculations on the related dimethylamino complex and its protonated form, as a model for complexed-Ca^{2+}, the emission changes are rationalized as a swap from ILCT (*p*-dialkylaminophenyl pyrazolate to pyridine) to LLCT (cyclometalated phenyl pyrazolate → *p*-dialkylaminophenyl pyrazolate) in **11-Ca^{2+}** complex. Similar titration experiments have been performed for the hard bivalent metal cations such as Mg^{2+}, Ba^{2+} and their association constants *K* were determined.

The heteroleptic iridium complex **12** (Scheme 3), in which the aza-15-crown-5 ether ionophores have been incorporated into the cyclometalated phenyl ring of the phenyl-2-pyridine ligands, showed on-off selective emission triggering by inhibition of photoinduced electron transfer (PET) upon binding of Mg^{2+} [44]. Statistical processing of the spectrophotometric data for **12** supported the formation of 1: 1 and 1: 2 (12: Mg^{2+}) species corresponding to the successive ligation of two metal cations to the two crown ether moieties.

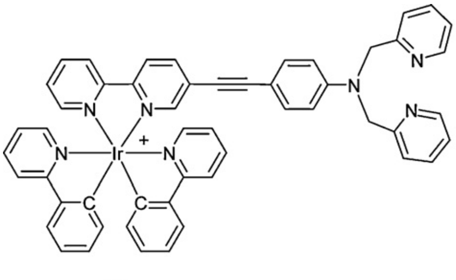
3. Metal complexes incorporating a di(2-picolyl)amine (2,2′-DPA) receptor

A number of molecular sensors combining the ionophore di(2-picolyl)amine (2,2′-DPA) and a fluorophore have been synthesized and characterized. Such systems are highly sensitive to the modification of their environment, leading to various optical responses. This allowed the detection of divalent metal cations such as Zn^{2+}, Cd^{2+} and Cu^{2+}, thanks to the interesting chelating properties of 2,2′-DPA [45–50]. The approach is generally based on a photoinduced electron transfer inhibition process in which the electron transfer from the nitrogen lone pair electrons of the DPA unit to the chromophore was blocked upon ion binding. For example, Peng et al. reported on a selective boradiazaindacene-based sensor for the fluorescent imaging of Cd^{2+} in living cells, via an internal charge transfer (ICT) mechanism [50].

More recently, the combination of 2,2′-DPA to various metal fragments (Ir, Au, Re, Pt) has proved to be a useful starting point for phosphorescent sensor design [51–54]. For example, this receptor unit has been incorporated to luminescent bis-cyclometalated Ir complexes, at the **3** and **4** position of the bipyridine ligand through an ethynyl or a vinyl π-linker, respectively [51,52].

Complex **13** is weakly luminescent (λ_{em} = 616 nm), it displays a short-lived, low-energy emission, whose likely origin is an excited state of primarily ILCT character centered on the functionalized 2,2′-bipyridyl ligand [51]. Complex **13** exhibits a remarkable *switching on* luminescence sensing effect to Zn^{2+}, Cd^{2+}, and Hg^{2+}: 30-, 27- and 24-fold increase ($I - I_0/I_0$) in emission intensity were observed upon titration with 1 equiv of Zn^{2+}, Cd^{2+} and Hg^{2+} in acetonitrile solutions, respectively (Fig. 4). The observed emission spectral changes were attributed to a conversion of the lowest energy excited state from ILCT to LLCT and MLCT character.

Guerchais et al. recently reported on a novel iridium complex **14** incorporating a styryl group substituted with a di(2-picolyl)amino (DPA) group and the changes to its optical properties upon binding Ni^{2+}, Zn^{2+} and Cd^{2+} (Fig. 5) [52]. The presence of Zn^{2+} ions specifically perturbs the excited state, giving rise to blue-shifted absorption and emission, and to a shorter luminescence lifetime.



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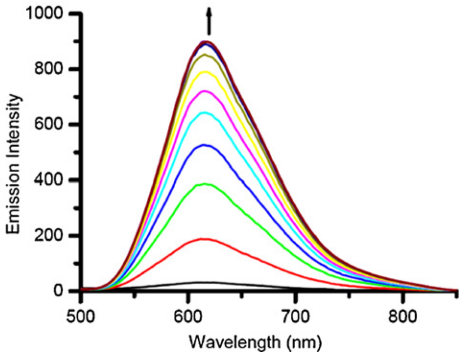
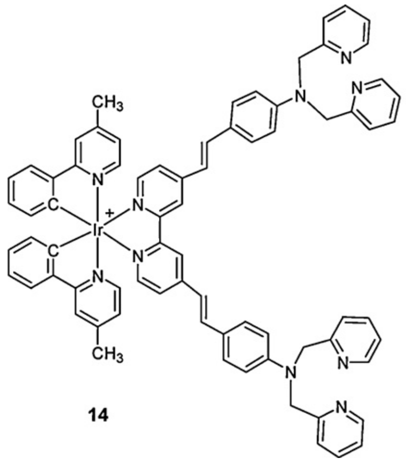


Fig. 4. Emission spectral changes (λ_{exc} = 360 nm) for **13** (20 μM) upon titration with Zn^{2+} (0–1.0 equiv) in MeCN. This figure was reproduced from Ref. [51] with permission of the copyright holders.



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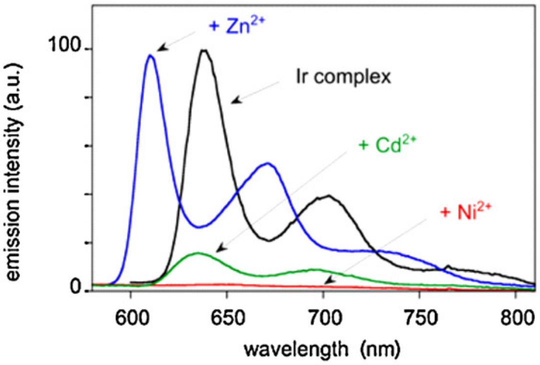


Fig. 5. Luminescence spectral changes (77 K) of **14** (conc. = 3 × 10^{-6} M) in ethanol–methanol (4:1, v/v) upon the addition of $M(ClO_4)_2$ (M = Ni, Zn, Cd) (conc. = 6 × 10^{-5} M); λ_{exc} = 385 nm (isosbestic point).

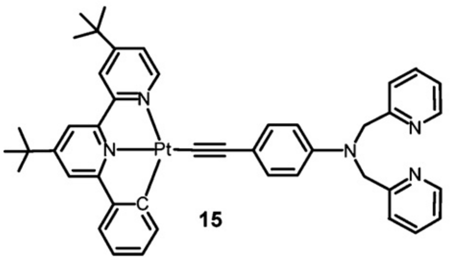
The emission (640 nm) of 14 at 77 K was completely quenched upon adding Ni^{2+} ions, whereas Cd^{2+} lead only to partial quenching and a scarcely perceptible blue shift (0.009 eV). Most strikingly, the coordination of Zn^{2+} ions induced a unique response: a blue-shifted emission (610 nm) of the intensity comparable to **14** (for excitation at the isosbestic point at 385 nm) with a lifetime of 34 μs was observed, indicative of the formation of a new emissive species. The stoichiometric ratio of the species formed between complex **14** and M^{2+} was estimated as 1:2 in accordance with the presence of two DPA receptors.

As in absorption, the emission blue-shift can be interpreted in terms of a stabilisation of the highest occupied molecular orbitals as the N lone pair becomes bound to the Zn^{2+} ion. That selectivity over Cd^{2+} is observed only in emission and not in absorption reflecting presumably a subtle difference in the electronic distribution in the triplet and singlet excited states. The selective blue-shift induced by Zn^{2+} implies that, in the excited state, the more charge-dense Zn^{2+} ion interacts more strongly with the amino group of the DPA unit than does Cd^{2+}.

With our ongoing interest in the design of (*C^N^N*-phenylbipyridine)platinum(II) acetylide complexes, we have designed and prepared a luminescent cyclometalated platinum complex **15** incorporating the host receptor DPA on the phenylacetylide ligand [55]. Complex **15** shows very weak emission (ϕ = 0.003, 298 K) at 550 nm in acetonitrile solution. We found that **15** is sensitive to the capture of various metal cations (Zn^{2+}, Cd^{2+}, Ni^{2+} and Pb^{2+}) leading to a change of luminescence, the intensity of which depends on the nature of the cation species. Upon addition of Zn^{2+}, Cd^{2+} and Pb^{2+}, the phosphorescence emission intensity of **15** exhibited enhancement, the importance of which depends on the metal cation (see Fig. 6 upon addition of Zn^{2+} cations).

The luminescence enhancement observed upon addition of Zn^{2+}, Cd^{2+}, and Pb^{2+} cations can be viewed as the shift of the non-emissive ^{3}LLCT to higher energies, as the acetylide based HOMO is stabilized upon coordination of metal cations. The ^{3}MLCT emissive state being the lowest-lying excited state gives rise to a ^{3}MLCT $d\pi(Pt) \rightarrow \pi^*(phbpy)$ emission.

Interestingly, the phosphorescence emission intensity of 15 exhibited 15-, 4- and 0.3-fold enhancements $(I - I_0/I_0)$, respectively upon addition of Zn^{2+}, Cd^{2+} and Pb^{2+} salts (Fig. 6). Such a contrast in the luminescence enhancements can indicate how strongly these cations effectively bind with the tertiary amine in the MLCT state. Cation interaction with the tertiary amine raises the energy of the LLCT state. It is reasonable to expect that the energy level of the LLCT state depends on the nature of the metal cation. Strong interaction as in $15\cdots Zn^{2+}$, in the excited state, will favor its ^{3}MLCT state that would decay via normal radiative and nonradiative paths. Weaker interaction with this tertiary amino nitrogen atom, as for Cd^{2+} and Pb^{2+} complexes with **15**, would allow a competition between the ^{3}MLCT and ^{3}LLCT states. The differences in the luminescence enhancements would thus reflect the binding mode of these cations with the DPA multidentate unit of **15**,



15

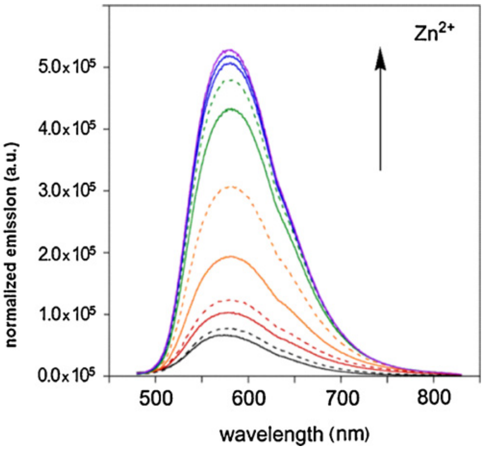


Fig. 6. Variation of the emission spectrum of **15** with $Zn(ClO_4)_2$ in CH_3CN solvent; [15] = 2.4 × 10^{-5} M; (3 mL) $[Zn(ClO_4)_2]$ = 1.2 × 10^{-3} M, addition 8 μL each time. Excitation at 445 nm (isosbestic point).

in the excited state, and more specifically with the tertiary amino group.

4. Metal complexes (Pt, Ir) as luminescent sensors for lead(II) and mercury(II) cations

4.1. Macrocyclic pyridine based platinum(II) complex

The design of neutral ligands, especially for binding guest molecules in polar solvents is a challenging goal, owing to competing solvent effects [56]. Pyridine groups are interesting complexation auxiliaries when present in the side-chain of macrocycles possessing hard base-type atoms such as crown ethers [57,58]. Jurczak et al. investigated the ion-binding properties of secondary amide-based macrocycles containing additional ether and pyridine groups toward alkaline-earth metal and heavy metal cations. Complexation of Pb^{2+} cations proceeds via the pyridine nitrogen and ether oxygen atoms [59]. This design concept was extended by us to a cyclometalated platinum complex. We found that the macrocyclic pyridine containing σ-alkynyl ligand of 16 acts as a selective lead(II) ion receptor that allows the photophysical properties of the $[(C^{\wedge}N^{\wedge}N)\mathrm{Pt}]$ moiety to be tuned (Figs. 7 and 8) [60].

The room-temperature emission spectrum of complex **16**, upon excitation into the MLCT band (λ_{exc} = 450 nm) exhibits a structurally unresolved spectrum with a maximum at 566 nm, and emission quantum efficiencies of the order of 7%. The emission of **16** is assigned to ^{3}MLCT excited states to which acetylide-to-diimine L′LCT transitions may also contribute. Complex **16** shows an *on-off* emissive effect in the presence of lead (II) ions perchlorate salts in MeCN at 298 K. A remarkable luminescence decrease at 570 nm (λ_{exc} = 450 nm) was observed upon addition of lead cations, while the shape, the lifetime and the energy of the emission band did not change (Fig. 8). The macrocycle acts via the nitrogen atom of the pyridine ring electronically connected to the Pt center via the $C{\equiv}C$ bond, this leads to a switch from L′LCT to ML′CT excited states upon complexation of lead(II) ions.

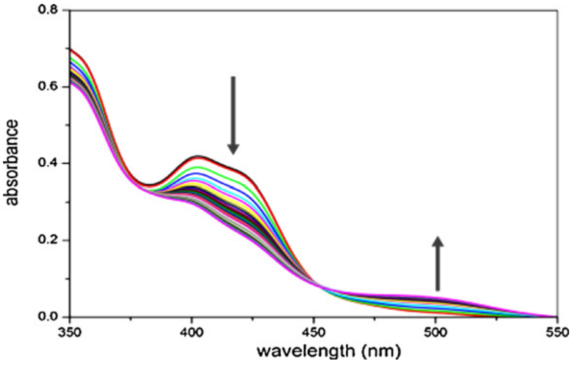


Fig. 7. Absorption spectral changes of 17 ([17] = 5.7 × 10^{-5} M in CH_3CN, 298 K) with $Pb(ClO_4)_2$ ($[Pb(ClO_4)_2]$ = 1.0 × 10^{-2} M, 1 μL added each time) as a function of Zn^{2+} concentration (0–5 equiv.).

The above observations suggest that the 1:1 complexation of Pb^{2+} cations occurs via the nitrogen atom of the pyridine ring and leads to a stronger electron-acceptor capability of the pyridine ring. We suggest that the new absorption band due to lead-complexed **16-Pb**$^{2+}$ could be assigned to an ML′CT [d $\pi(Pt) \rightarrow \pi^*(C{\equiv}C\text{-py})$] transition. This non-emissive state becomes the lower-lying excited state, as the result of the lowering of the energy of the π^* orbitals of the $C{\equiv}C$-py fragment upon lead binding, i.e. a switch of CT to the opposite direction.

4.2. Flavone-based platinum(II) complexes

In a development of previous research on the use of ruthenium alkynyl derivatives as chemosensors, Fillaut has reported on a fluorescent sensor based on the association of a flavonol moiety with a ruthenium complex. The combined use of the 3-hydroxyflavone unit as a receptor for the metal cations, and of a phenylacetylide ruthenium moiety provides an efficient molecular sensor for rapid, sensitive and selective detection of lead(II) cations [61].

This strategy was then extended to the platinum complexes $[Pt(C^{\wedge}N^{\wedge}N\text{-tBu}_2\text{-phpy})(C{\equiv}C\text{-FLV-3-OR})]$ (FLV denotes the flavone-based receptor) 17 (a, $R{=}CH_3$; b, $CH_2CH_2OCH_3$; c, $(CH_2CH_2O)_2CH_3$) [62]. All three complexes **17a–c** emit intense luminescence. The observed emission lifetimes of ~20 μs are much longer than those of related complexes without the flavone unit [27], despite the emission being in the same region. This suggests that the emissive excited state has substantial $^3IL(C{\equiv}C\text{–FLV-3-OR})$ character, with the metal making a smaller contribution to the HOMO than it does in the related $[Pt(C^{\wedge}N^{\wedge}N)(\text{–}C{\equiv}C\text{–Ar})]$ compounds.

Dramatic change in the emission spectrum of **17b** upon binding of Pb^{2+} was observed. Addition of increasing concentrations of Pb^{2+} to 17b in CH_3CN led to the appearance of a new, blue-shifted, structured band centered, while the intensity of the initial band concomitantly decreased (Fig. 9).

Modifications (λ, τ) in the emission spectrum of **17b** upon binding of Pb^{2+} evidence a profound modification in the excited

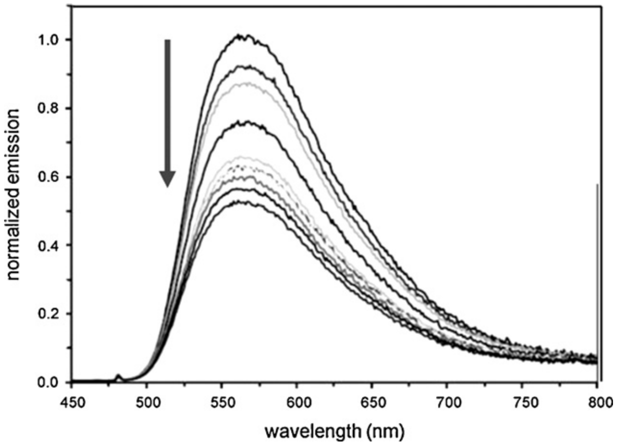


Fig. 8. Variation of the emission spectrum of **17** with $Pb(ClO_4)_2$ in CH_3CN solvent; [17] = 5.7 × 10^{-5} M; (3 mL) $[Pb(ClO_4)_2]$ = 1.0 × 10^{-2} M, addition 3 μL each time. Excitation at 450 nm (isosbestic point).

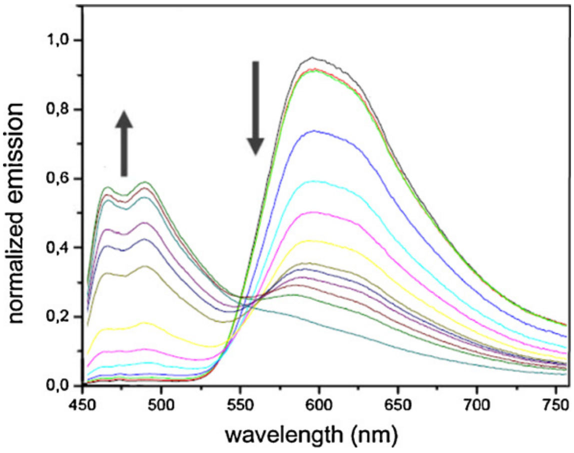


Fig. 9. Variation of the emission spectrum of **17b** with $Pb(ClO_4)_2$ in MeCN solvent; [17b] = 5.0 × 10^{-6} M; (3 mL) $[Pb(ClO_4)_2]$ = 1.0 × 10^{-2} M, addition 3 μL each time. Excitation at 393 nm (isosbestic point).

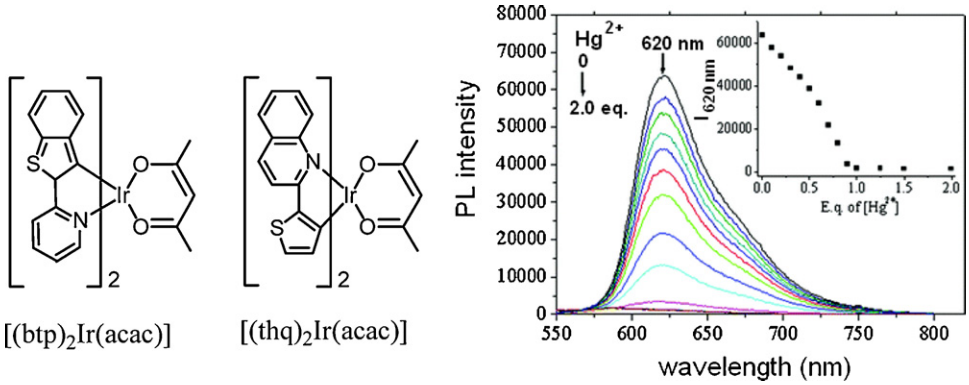
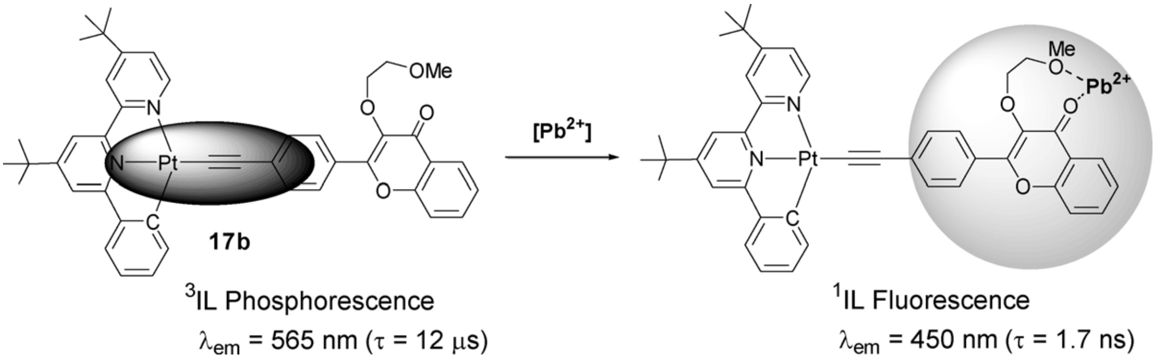


Fig. 10. (right) Changes in the luminescence spectra of $[Ir(thq)_2(acac)]$ (20 μM) in air-equilibrated MeCN solution with various amounts of Hg^{2+} ions (0–40 μM); λ_{exc} = 375 nm. Inset: titration curve of $[Ir(thq)_2(acac)]$ with Hg^{2+}.

state properties of the molecule. These changes can be tentatively rationalised in terms of binding of Pb^{2+} leading to a decrease in the energy of the highest-occupied flavone-localised orbitals. This would result in blocking the internal conversion from the ^{3}MLCT to ^{3}IL and leads to fluorescence from the singlet state (^{1}IL) of the flavone. This work demonstrates an unprecedented switch between triplet and singlet emission, upon metal binding.



4.3. *Sulfur-based iridium complexes*

Huang et al. have demonstrated a selective colorimetric, electrochemical and phosphorescent mercury chemosensor based on the iridium(III) complexes $[Ir(btp)_2(acac)]$ and $(thq)_2Ir(acac)$ [63,64]. The addition of Hg^{2+} on $[(thq)_2Ir(acac)]$ induced a pronounced *on/off*-type phosphorescent signaling behavior, which could be observed by the naked eye. Hg^{2+} is coordinated with $[Ir(thq)_2(acac)]$, forming a 1: 1 complex. The interaction between Hg^{2+} and the sulfur atom of the cyclometalated ligands is responsible for the significant variations in optical and electrochemical signals. According to Pearson's hard–soft acid–base theory, Hg^{2+} is a thiophilic metal ion and soft Hg^{2+} ions (soft acid) can interact preferentially with sulfur (a soft base).

Only the addition of Hg^{2+} resulted in a prominent luminescence change, whereas addition of a large excess of other competitive cations (such as Mg^{2+}, Cr^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+} and Cd^{2+}) caused only slight luminescent changes, confirming that $(thq)_2Ir(acac)$, displayed a high selectivity in sensing Hg^{2+} (Fig. 10).

Coordination of Hg^{2+} with the sulfur atom of $Ir(btp)_2(acac)$ led to a blue-shift of emission spectrum. The different emission responses of the above two complexes to Hg^{2+} was tentatively assigned to the significant difference in charge distribution. The strong decrease of the emission for $Ir(thq)_2(acac)$ after binding with Hg^{2+} can be explained in terms of electron transfer between the excited complex to the complexed mercury cation.

5. Concluding remarks

In conclusion, this paper illustrates the various strategies through the emissive studies of selected complexes which contain functionalized ligands with specific receptors R for heavy and transition metal cations. Both families of cyclometalated platinum(II) and iridium(III) complexes emerge as promising candidates for monitoring the environment, thanks to their photoluminescence properties. Introducing appropriate receptors, on the polyimine or the ancillary acetylide ligands for the detection of metal cations appears particularly well adapted for inducing changes in their emission properties. This article also shows that the design of the use of phosphorescent metal (Ir, Pt) complexes–based chemosensors is not limited to the interaction of crown ethers with metal cations, metal-based chemosensors for transition- and heavy-metal ions have been developed during the last decade. Interestingly, on the basis of these models, phosphorescence turn-on or turn-off effects as well as changes in the emission wavelength and/or emission lifetime could be applied for designing phosphorescent probes of specific targets.

Most of the reported examples of metal-based chemosensors have been used in organic or organic/aqueous solutions, probably as the result of the low water solubility of metal complexes. Although this research is of fundamental importance, the development of luminescent probes that are appropriate for detection in pure aqueous solution has to be achieved. Therefore, the new challenges deal with the design and synthesis of water-compatible chemosensors, as far as for the determination of the presence of the metal cations in the environment (Zn^{2+}, Cd^{2+}, and Hg^{2+}...) is concerned.

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