Anion recognition and sensing by transition-metal complexes with polarized N-H recognition motifs

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Abstract

Transition-metal complexes for anion recognition and sensing have attracted increasing attention due to their rich spectroscopic and luminescent properties upon interacting with anions. In this review, we summarize the recent progress made with transition-metal complexes for anion sensing purposes. We focus on ruthenium(II), rhenium(I) and iridium(III) polypyridyl complexes with different polarized N–H recognition motifs acting as the anion receptors.

1. Introduction

The development of specific chemosensors for the efficient detection of anions is an important subject in the field of supramolecular chemistry due to their fundamental roles in biological, environmental, and chemical processes [1-8]. Compared to the well developed field of cation binding and sensing, anion recognition is a more challenging field because of the variable size, shape, and strong solvation of the species [9]. As anions are larger than their isoelectronic cations and, thus, have a smaller charge-to-radius ratio, electrostatic interactions are less effective for anions than their corresponding isoelectronic cations [10-12]. Solvation effects are also more prominent for anions and this is an important factor to consider in designing artificial anion receptors. Hydroxylic solvents usually form strong hydrogen bonds with anions and this will reduce the affinity of anions toward anion receptors. It is, therefore, particularly challenging to design a synthetic receptor to bind anion in a pure aqueous environment due to the strong competitive hydrogen-bonding interaction with water. Hydrophobicity can also influence the selectivity of an anion receptor, as hydrophobic anions tend to bind more tightly to the hydrophobic sites of the receptors. Therefore, to achieve the desired sensitive and selectivity, the combination of electrostatic attraction, hydrogen bonding, hydrophobic effects, and stacking interactions all need to be taken into consideration when designing artificial anionic hosts [13]. In the design of anion receptors, various non-covalent interactions, such as electrostatic, hydrogen bonding, coordination to the metal center, hydrophobicity, and any combination of these, need to be utilized [14-21].

Among the various designs of synthetic receptors, the incorporation of luminescent chromophores, which are sensitive to interactions between the host and guest molecules, into a receptor has recently gained considerable attention due to their high sensitivity and low detection limit [22-30]. The appeal of chemosensors that contain luminescence chromophores stems from the high sensitivity of luminescence detection compared to other spectroscopic methods. The binding of anionic species to the recognition sites often introduces new optical transitions or excited states and leads to changes in certain photophysical properties of the receptors by (such as their absorption spectra, luminescence intensity, or lifetime, etc.), which can then serve as an indicator of guest association.

For the anion receptors based on hydrogen bonding interactions, a number of organic compounds with the polarized N–H functional groups, such as pyrrole, imidazole, urea, sulfonamide, amide, thioamide and thiourea moieties, that are

capable of providing a hydrogen bonding interaction to certain anions. In general, hydrogen bond-induced π -electron delocalization or basic anion induced N–H deprotonation, which highly depends on the acidity (pK_a) of the N–H proton in a receptor, serves as the signaling output of the anion-receptor interaction. The pK_a values of a polarized N–H proton in a receptor usually can be determined by spectroscopic titration of the receptor by appropriate bases. However, organic molecules generally have small Stokes shifts, which can interfere with the data collection due to the intrinsic inner filter effect, and also sometimes limited photostability.

Incorporating a transition metal into the framework of sensory systems offers several advantages over pure organic counterparts. Firstly, transition-metal complexes are often positively charged or electron deficient in nature. This property leads to either the enhancement of the electrostatic interactions with negatively charged species or a higher probability of orbital overlap and, thus, stronger bonding interactions with anionic species. Secondly, transition-metal complexes typically possess precisely defined geometries. This characteristic is especially useful for enhancing the selectivity of certain shaped anions or inducing unusual structural changes upon binding to anions. Thirdly, and perhaps the most appealing reason, is that transition-metal complexes possess a variety of unique functionalities such as redox activity, spectroscopic features in the visible region (i.e., color), magnetism, luminescence, and catalytic ability. Incorporation of these functionality properties into the sensory system provides for not only the improvement of sensor technology but also some other guest recognition based applications, such as anion transport, drug delivery, and catalysis.

Based on the above advantages, many transition-metal complexes have been extensively studied as luminescent anion chemosensors in the last two decades [31-66]. Herein, we focus our attentions on the ruthenium(II), rhenium(I) and iridium(III) polypyridyl complexes with different types of polarized N–H recognition motifs and highlight their unique properties for anion recognition and sensing. This review is not intended to comprehensively cover all reported anion probes based on metal complexes, but will focus on some selective and illustrative examples.

2. Ruthenium(II) complexes for anion sensing

The $[\text{Ru}(\text{bpy})_3]^{2+}$ unit is known to display unique photophysical and redox properties [67-68]. In 1993, Beer and co-workers prepared the first ruthenium(II) complexes for anion sensors utilizing the $[\text{Ru}(\text{bpy})_3]^{2+}$ unit as a chromophore and bipyridyl ligands bearing amide substituents as the anionic recognition site [69]. The ruthenium(II)

bipyridyl moiety in combination with amide groups has been incorporated into acyclic, macrocyclic, and calix[4]arene structural frameworks to produce a class of chemosensor for various anions [70-80].

2.1 Pyrrole-based Ru(II) complexes as chemosensors

Pyrrole and its derivatives are one of the most investigated anion receptors [81-83]. Pyrrole is a weak acid and the unsubstituted pyrrole has a pK_a of 23, which means it can form hydrogen bonds with anions but can also be deprotonated by strong bases [82]. Thus, it can be introduced into the ligand of Ru(II) complexes to act as an anion receptor.

Sessler and co-workers reported the synthesis and anion binding properties of the dipyrrolylquinoxaline (DPQ) phenanthroline-based ruthenium(II)-polypyridyl complex **1** [84]. The coordination of Ru(II) makes the free ligand DPQ-phenanthroline electron-deficient and renders the N-H protons of the pyrrole more acidic compared to the free ligand, thereby promoting the key anion-to-DPQ interactions. The Ru(II) complex **1** displayed a fluoride anion affinity that is higher than free ligand DPQ-phenanthroline, giving a binding constant for fluoride of $12,000\text{ M}^{-1}$ by UV-vis spectrophotometry in a DMSO solution (*ca.* 30 times higher than the free ligand).

Later, the same group appended dipyrrole groups to one of the ligands in $[\text{Ru}(\text{bpy})_3]^{2+}$ to generate the Ru(II) complex **2** for emission-based selective detection of dihydrogen phosphate [85]. The emission intensity of complex **2** at 630 nm gradually decreased as the dihydrogen phosphate concentration increased from 0 to $9.5\text{ }\mu\text{M}$. A binding constant of $1.0 \times 10^5\text{ M}^{-1}$ was calculated through fluorescence titration carried out in a DMSO solution. The Job plot experiment revealed a 1:1 complex for **2** with dihydrogen phosphate.

The development of emission lifetime-based chemical sensing is particularly attractive because this detection method is unaffected by excitation source intensity fluctuations, light loss in the optical path, light scattering, and detector drift, thereby circumventing many limitations of emission intensity-based methods. Anzenbacher and co-workers prepared the first luminescence-lifetime based sensor for anions utilizing Ru(II) complex **3**, containing a DPQ-phenanthroline receptor [86]. In the presence of anions, the photoluminescence intensity of **3** was strongly quenched by fluoride and cyanide. The binding constants were determined to be $6.4 \times 10^5 \text{ M}^{-1}$ and $4.3 \times 10^5 \text{ M}^{-1}$, respectively, in acetonitrile solutions. Furthermore, anion-induced luminescence lifetime changes can be observed and the lifetime shortens as a function of the anion concentration.

2.2 Imidazole-based Ru(II) complexes as chemosensors

Similar to pyrrole, the polarized N–H proton of imidazole can also serve as an anion interacting motif via hydrogen bonding interaction. Thus, it can be introduced into the ligands of transition-metal complexes to facilitate the recognition and binding of anions [61-66].

A series of Ru(II) complexes **4–7** containing the Ru(II)-bipyridine moiety as a chromophore and the 2,2'-bisimidazole-like ligand as an anionic recognition site has

been synthesized and investigated by Ye and co-workers [87-90]. Interestingly, the bisimidazole unit is a bifunctional unit, which possesses both electron lone pairs for coordination to the central metal ion as well as an N-H group for hydrogen bonding to anions in the second coordination sphere. The investigation indicated that the optical absorption, emission, and redox potential of the Ru(II) complexes **4–7** all depend upon the N-H protonation state of the bisimidazole-like ligand. Three states of the bisimidazole-like ligand exist, namely the formation of hydrogen bonds between the N-H protons and the anions, the mono-deprotonated ligand and the double-deprotonated species. These may be controlled by several factors: (i) the acidity of the metallo-receptor, (ii) the basicity of the anion, and (iii) the strength and number of hydrogen bonds. The binding strength is highly related to the charge numbers and the match of molecular shape between the hydrogen-bonding donor and the acceptor groups. For instance, complex **4** donated two N-H protons for hydrogen bonding to Cl^- , Br^- , I^- , NO_3^- , HSO_4^- , H_2PO_4^- , and OAc^- anions. The N-H proton of complex **4** was further deprotonated in the presence of excess OAc^- anion and changed color from yellow to orange brown [87]. However, the fluoride ion has a high affinity toward the N-H protons of the bisimidazole-like ligand for proton transfer, rather than simple hydrogen bonding; because of the formation of the highly stable HF_2^- anion. This resulted in stepwise deprotonation of the two N-H protons and it was noticeable that the color changed from yellow to orange-brown, and then to violet (see Scheme 1 and Fig. 1).

Scheme 1. Schematic representation of the interaction between sensor **4** and various anions. Reproduced with permission from Ref. [87].

Fig. 1. Color changes observed for **4** in MeCN solution (8×10^{-5} M) and the addition of 1 equiv of the corresponding anions as TBA salts and 6 equiv of TBAF.

Reproduced with permission from Ref. [87].

Subsequently, the Ye group reported the ruthenium(II) 2,2'-bisbenzimidazole complex **5** as an anion receptor [88]. Being different from complex **4**, this investigation suggested that complex **5** interacted with the Cl^- , Br^- , I^- , NO_3^- , HSO_4^- ,

and H_2PO_4^- ions via the formation of hydrogen bonds. Complex **5** underwent a stepwise process with the addition of fluoride and acetate anions: formation of the mono deprotonated complex with a low anion concentration followed by the double-deprotonated complex in the presence of a high anion concentration. It also displayed distinguishable responses to $\text{CCl}_3\text{CO}_2^-$ and CF_3CO_2^- anions. The different anion binding affinity between complexes **4** and **5** may be mainly attributed to their different $\text{p}K_a$ values of 7.2 and 5.7 for complexes **4** and **5**, respectively. The 2,2'-bisbenzimidazole motifs acted as electron-withdrawing groups in **5**, rendering the N-H protons more acidic and providing a different behavior toward carboxylate anions.

Based on the above study, Ye *et al.* designed and synthesized the ruthenium(II)7,7'-dimethyl-2,2'-bisbenzimidazole complex **6** [89]. Complex **6** displayed an intermediate $\text{p}K_a$ value of 6.2, compared to 7.2 for complex **4** and 5.7 for complex **5**. This moderate acidity was significant for sensing weakly basic anions. Thus, complex **6** displayed strong hydrogen bonding interaction with weakly basic anions, such as Cl^- , Br^- , I^- , or NO_3^- and HSO_4^- , with binding constants between 17,000 and 21,000 M^{-1} in CD_3CN . Upon binding of weakly basic anions, the emission intensity at 617 nm was enhanced by about 35–40% accompanied with a minor red shift in the emission maximum. The enhancement of the emission intensity was attributed to the rigidifying effect of hydrogen bonding on the N-H bond, which reduces the non-radiative decay of the $^3\text{MLCT}$ state through the N-H pathway. On the other hand, strongly basic anions, such as F^- and AcO^- , deprotonated two N-H protons of the imidazole groups, reducing the luminescence intensity through intramolecular quenching of the emissive $^3\text{MLCT}$ state by electron transfer from the double-deprotonated complex **6**.

The Ye group has also reported a ruthenium(II) bisimidazole-like complex **7** with highly acidic N-H protons and two “chelating” N-H...O intramolecular hydrogen bonds as the anion receptor [90]. Complex **7** underwent deprotonation in acetonitrile upon addition of strong basic anions, such as F^- and OAc^- . For weakly basic anions, complex **7** showed strong affinity towards Cl^- and Br^- anions, is bound weakly to I^- anion, and has no apparent affinity toward NO_3^- and HSO_4^- anions. These studies demonstrate that the hydrogen bonding affinity of these complexes **4–7** toward anions can be fine-tuned by small changes to the peripheral groups of the anion binding site in order to achieve the desired acidity for anion detection and discrimination.

The ferrocene-imidazophenanthroline-based ruthenium(II)-polypyridyl complex **8** was designed and synthesized by Molina and co-workers [91]. Interestingly, complex **8** showed an extreme selectivity toward Cl^- anion over all other anions examined through two channels: cathodic redox shift of the Fe(II)/Fe(III) redox

couple (see Fig. 2) and a significant emission enhancement compared to other anions (see Fig. 3). The spectra of electrochemical, absorption, emission, and ^1H NMR strongly indicated a hydrogen bonding interaction between the imidazole N–H proton and the bound chloride.

Fig. 2. Changes in redox properties of complex **8** (1 mM) in CH_3CN (black) upon addition of 1 equiv of Cl^- (blue). Reproduced with permission from Ref. [91].

Fig. 3. (a) Changes in the fluorescence emission spectrum of complex **8** upon titration with Cl^- in CH_3CN . (b) Fluorescence intensity increase of **8**, in relation to the free ligand, after addition of 1 equiv of several anions in CH_3CN . Reproduced with permission from Ref. [91].

Recently, Ye and co-workers reported imidazole-based Ru(II) complexes **9-13** for anion sensors [92]. Only complexes **9** and **13** displayed high selectivity toward cyanide anion without interference from other common anions in water, including fluoride and acetate. Appropriate acidity of the N–H proton and multipoint hydrogen bonding interactions are both important in enhancing the selectivity and sensitivity toward CN^- ion in water. The bimetallic ruthenium(II) complex **13** possessed an appropriate $\text{p}K_{a2}$ value for the N–H proton and a C-shape cavity structure with three-point hydrogen bonding donating to CN^- , consisting of N–H and phenyl C–H hydrogen bonds. The detection limit is as low as 5 μM in water. These authors have also reported the first sensor based on the direct observation of CN^- induced emission lifetime changes in water, and applied the HMBC (heteronuclear multiple bond correlation) technique to directly investigate the binding site of the receptor toward CN^- via hydrogen bonding.

The bimetallic ruthenium(II) complexes **13** and **14** were also reported by the Baitalik group [93-94]. The metalloreceptors containing two imidazole N–H protons in the second coordination sphere, which became appreciably acidic due to metal coordination, can be utilized for recognition of selective anions such as F^- , AcO^- and H_2PO_4^- ions. Interestingly, the emission intensity and lifetime of these complexes were decreased by F^- and AcO^- ions, while increased by H_2PO_4^- in CH_3CN . These results suggested that in the presence of excess F^- and AcO^- ion, deprotonation of the

imidazole N–H protons of complexes occurred. Complexes **13** and **14**, however, interacted with H_2PO_4^- via the formation of hydrogen bonds.

Wang and co-workers designed and synthesized a bifunctional Ru(II) complex **15** with a phenanthroline moiety coordinated to a Ru(bpy)₂ fragment as the first coordination sphere, and the imidazole N–H proton and uncoordinated terpyridine moiety as the second-coordination sphere for the recognition of anions and cations [95]. The complex **15** exhibits an efficient turn-on emission for H₂PO₄[−] and an emission turnoff for F[−] and OAc[−] ions. In addition, complex **15** showed a highly selective colorimetric response for Fe²⁺ ion.

Baitalik and co-workers utilized a 4,5-bis(benzimidazol-2-yl)imidazole scaffold

to construct monometallic and bimetallic ruthenium(II) complexes **16** and **17** as the colorimetric sensors for anions [96]. Complexes **16** and **17** contain three and two N–H protons, respectively, that could be donated for hydrogen bonding to the anions. Both of the metalloreceptors are selective to F^- and AcO^- ions, which can be detected by a color change to the naked eye. At lower concentration of anions, a 1:1 hydrogen-bonded adduct was formed. However, stepwise deprotonation of the imidazole N–H protons occurred at higher concentrations of anions.

Later, the same group synthesized the ruthenium(II) complex **18** derived from the Ru(II)-bipyridine moiety as a chromophore and imidazole-4,5-dicarboxylic acid as an anion receptor site [97]. The luminescence of **18** was enhanced by addition of F^- , AcO^- and H_2PO_4^- ions. The emission intensity was significantly enhanced with a red shift of the emission maximum from 690 to 740 nm. In the presence of excess of anions, deprotonation of the N–H proton on the imidazole occurred and was accompanied by a distinct change of color.

2.3 Urea-based Ru(II) complexes as chemosensors

The urea groups can also act as the anion receptors. Das and co-workers reported the urea-based ruthenium(II) complex **19** as an anion sensor [98]. The emission of complex **19** was strongly quenched by F^- , AcO^- and H_2PO_4^- ions, which is attributed to a faster decay of the excited triplet state upon anion binding because of the narrowing of the energy gap between the excited triplet and ground singlet states. The incorporation of a urea moiety into a Ru(II)-polypyridyl complex **20** was synthesized by Gunnlaugsson and co-workers [99]. Interestingly, the MLCT emission of complex **20** was sensitive to the binding of acetate, phosphate and pyrophosphate, but not fluoride, in CH_3CN . Furthermore, the metalloreceptor can distinguish between phosphate and pyrophosphate with an emission “turn-on” sensor for H_2PO_4^- and an emission “turn-off” sensor for $\text{HP}_2\text{O}_7^{3-}$.

2.4 Sulfonamide-based Ru(II) complexes as chemosensors

Among the various polarized N–H functional groups, sulfonamide represents a less explored class for anion sensing. The anion-sensitive bis(sulfonamide) functionality can be easily modified to incorporate coordinating dipyridyl or phenanthroline moieties. Previously, Sun and co-workers designed and synthesized the Ru(II) complex **21** featuring bis(sulfonamide) interacting sites incorporating highly chromophoric π -conjugated quinoxaline moieties as an anion probe [100]. A stepwise process was observed in the UV-vis spectral titration with F^- in DMSO. The spectral changes in the first process are attributed to the formation of a hydrogen-bound complex followed by proton transfer in the second process. The Job plot revealed a 1:1 complex for receptor with fluoride. These results implied that only one sulfonamide ligand interacts with the incoming anions. It is believed that the coordination of Ru(II) greatly facilitates the N–H proton dissociation in a polar DMSO solution. Therefore, the metalloreceptor **21** became a neutral molecule with two N–H protons dissociated at two different ligands that rendered only one intact sulfonamide N–H left available for anion interaction.

The sulfonamide-based ruthenium(II) complexes **22** and **23** were reported by the Lin group [101]. The complexes displayed strong affinity for F^- or AcO^- ions,

compared to the other anions. In general, the benzene-substituted complex **23** bound anions more strongly than the toluene derivative **22** did. The relatively lower binding affinity of the toluene-functionalized receptor was attributed to the electron-donating ability of the methyl group relative to the hydrogen atom of the benzene derivative.

3. Rhenium(I) complexes for anion sensing

Similar to the [Ru(bpy)₃]²⁺ units, the easy synthesis and diversified structural variations of rhenium(I) tricarbonyl diimine units have also been extensively studied as chromophores for anion sensing in the literatures [30, 43, 57].

3.1 Amide-based Re(I) complexes as chemosensors

Fundamental work by Lees and co-workers reported the designed and synthesized a series of luminescent rhenium(I) carbonyls complexes **24-27** with polarized N–H protons in amide groups as anion receptors [102, 103]. The N–H protons of complexes **24** and **25** exhibited chemical shift of 10.59 and 11.06 ppm in CDCl₃, respectively. The highly downfield chemical shift indicated the presence of strong intramolecular hydrogen bonding between the N–H protons and the nitrogen of the central pyridine. These results indicated that the tweezer amide bridged rhenium(I) complexes **24** and **25** contained the approximate right angle geometries [104, 105], and rendered them as effective anion receptors through hydrogen bonding. However, in the cases of complexes **26** and **27**, there was no chance to form intramolecular hydrogen bonding, but there may be intermolecular hydrogen bonding between the

amide protons and the carbonyl groups. This idea was tentatively supported by the slightly downfield shifting of the amide protons at 8.96 and 9.10 ppm for complexes **26** and **27**, respectively. The anionic sensory system studied comprises an amide–pyridine moiety, which provides the anion binding site through amide-anion hydrogen bonding and a signaling unit which is (4,4'-*t*Bu₂bpy)Re(CO)₃. The positive-charged character of the (4,4'-*t*Bu₂bpy)Re(CO)₃ moiety is also expected to provide an additional electron-withdrawing effect on the amide binding site. Fig.4 showed a typical 1:1 titration curve for the luminescence intensity upon addition of F⁻ to a degassed CH₂Cl₂ solution of complex **24**. Concomitant with the quenching, the luminescence maximum red shifts approximately 200–340 cm⁻¹ in each case. The lowest-energy band (¹MLCT) in the absorption spectrum also red shifts 670–1800 cm⁻¹ in each case along with the decrease of the π–π* band at 281 nm, and a new band developed around 347 nm with a shoulder around 436 nm upon addition of anion into the receptor solution (see Fig. 5). The red shift of the absorption and emission spectra is attributed to the formation of hydrogen-bonding interaction between the amide N-H and anions, which provides increasing electron donating ability of the bridging ligand and facilitates stronger MLCT transition in the anion-bound complex. The bathochromic shift of the MLCT band likely results in faster nonradiative relaxation because of better vibronic overlap between the emitting excited state and ground state that quenches the original ³MLCT emission, which is known as the energy gap law. The complexes **24** and **25** displayed high affinities toward halides, cyanide, or acetate anions with binding constants as high as 10⁴–10⁵ M⁻¹, only moderate binding affinity toward dihydrogen phosphate, and very weak binding affinity to nitrate or perchlorate anions. Importantly, the sensitivities of the metalloreceptors **24** and **25** are so high that the emission intensity can be effectively quenched by as much as 10%, even in the presence of only 10⁻⁸ M cyanide or fluoride anions.

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Fig.4. Titration curve of the addition of F^- anion monitored by luminescence spectroscopy. The inset showed the change of the emission intensity of complex **24** in CH_2Cl_2 solution upon addition of F^- anion. The emission spectra of the two lowest anion concentrations were not included for clarity. The excitation wavelength is 360 nm. Reproduced with permission from Ref. [103].

Fig.5. Changes in the absorption spectra of complex **24** ($6.7 \times 10^{-6} \text{ M}$) in CH_2Cl_2 solution upon addition of F^- anion. Reproduced with permission from Ref. [103].

The pioneering work by Beer's group on by rhenium(I) bipyridyl tricarbonyl interlocked rotaxanes has shown anion binding ability toward hydrogensulfate, chloride, and nitrate anions [106]. The rotaxane molecule **28** displayed emission enhancement upon titration of chloride, nitrate, and hydrogensulfate anions. The complementary topology and dimension of rotaxane molecule **28** has shown preferred selectivity to tetrahedral hydrogensulfate over chloride and nitrate anions. A similar effect by the rotaxanemolecule **29** also demonstrated high bind affinity toward chloride and hydrogensulfate in aqueous acetone solutions (9:1 acetone/water) with binding constant to chloride and hydrogensulfate up to 1.2×10^4 and $7.6 \times 10^3 \text{ M}^{-1}$, respectively [107].

3.2 Thioamide- and thiourea-based Re(I) complexes as chemosensors

Recently, Lees *et al.* reported a series of thioamide and thiourea bridged dinuclear rhenium(I) diimine tricarbonyl complexes **30** and **31** as luminescent anion sensors [108]. Luminescence intensity of the thioamide-based rhenium(I) complex **30a** was strongly quenched by F^- , Cl^- and Br^- ions. The thiourea-based rhenium(I) complex **31c** emits strongly at 575 nm and weakly at 465 nm upon excitation at 385 nm. The low-energy emission originates from a 3MLCT transition, while the high-energy band is tentatively assigned as a $^1\pi-\pi$ emission. Emission titration studies were carried out with I^- in CH_2Cl_2 at 298 K. The relatively strong emission peak at 575 nm showed quenching, while the initially less emissive band at 465 nm exhibited significant enhancement resulting in the formation of an isoemissive point at 530 nm (see Fig. 6). The origin of such spectral changes is not clear but may involve a substitution of the thiourea ligand by iodide. The association constant was calculated to be $2.96 \times 10^4 M^{-1}$ via a Stern–Volmer plot. 1H NMR titrations studies of compounds **30a** and **31a** with fluoride showed significant chemical shift changes of N–H protons of the thioamide and the thiourea, respectively. This is indicative of strong hydrogen bonding interactions between the N–H groups and the anions.

Fig. 6. Emission titration spectra of complex **31c** (1.0 × 10⁻⁵ M) in CH₂Cl₂ at 298 K with increasing concentrations of I⁻: (a) the initial spectrum without added anion, (b) 0.5, (c) 1.0, (d) 2.0, (e) 2.5, (f) 3.0 (g) 3.5, (h) 4.0, (i) 4.5, (j) 5.0, and (k) 5.5 equiv. Excitation wavelength is 385 nm. Reproduced with permission from Ref. [108].

3.3 Sulfonamide-based Re(I) complexes as chemosensors

The Sun group designed and synthesized quinoxaline bis(sulfonamide) bridged rhenium(I) complex **32** as an anion sensor [100]. UV-vis titration studies of the complex **32** were carried out with anions in CH₃CN. Two-step equilibrium phenomena were also observed in the titration of F⁻, CN⁻ and OAc⁻ ions. Job plots confirm the 1:2 stoichiometry between **32** and these anions. However, upon the addition of H₂PO₄⁻ or Cl⁻ ions, only a single equilibrium was observed in the UV-vis absorption response and the Job plots show a 1:1 stoichiometry for both anions. The stepwise process observed in the spectrophotometric titration with F⁻ can be described by two stepwise equilibria: (1) formation of a hydrogen-bound complex via

sulfonamide N–H protons with an incoming anion, followed by (2) deprotonation of the acidic sulfonamide N–H proton to form the mono-deprotonated complex **32** and HF_2^- . In the cases of CN^- and OAc^- , the complex **32** underwent a stepwise double proton transfer. The less basic H_2PO_4^- and Cl^- ions showed no ability to deprotonate the sulfonamide N–H protons, thus, formed only simple 1:1 hydrogen bonding complexes with complex **32**.

3.4 Acetylamino- and trifluoroacetylamino-based Re(I) complexes as chemosensors

Ko and co-workers reported the synthesis, photophysics, and anion-sensing properties of a series of luminescent rhenium(I) complexes **33–35** with acetylamino- and trifluoroacetylamino-functionalized 1,10-phenanthroline ligands [109]. These complexes displayed selective luminescence quenching with CN^- , F^- and AcO^- anions. The luminescence quenching can be ascribed to intramolecular quenching of the emissive $^3\text{MLCT}$ state through the electron-transfer mechanism from the anionic deprotonated amide moiety.

3.5 Catecholamide-based Re(I) complexes as chemosensors

The catecholamide-based rhenium(I) complexes **36** and **37** were reported by

Duhme-Klair's group [110, 111]. These complexes showed highly selective for the biologically relevant oxometalates such as molybdate, tungstate, and vanadate. Upon the addition of molybdate, the emission intensity of **36** decreases almost linearly until a ratio of sensor-to-molybdate of approximately 2:1 is reached (see Fig. 7). This ratio is consistent with the predominant formation of *cis*-dioxo-Mo^{VI}-dicatecholate complexes. Although not being discussed by the authors, the emission quenching of complex **36** likely originates from introducing a low-lying nonemissive ligand-field excited state upon molybdate binding. The detection limit was determined to be 55 $\mu\text{g L}^{-1}$ in a 95:5 acetonitrile/water solution at pH 4.

Fig.7. Emission spectra of **36** (10⁻⁴ M) in the presence of increasing concentrations of molybdate (in aqueous acetonitrile at pH 4.0, buffer: 2,6-lutidine, excitation wavelength is 370 nm). Inset: Emission intensity at 565 nm as a function of molar equivalents of MoO₄²⁻. Reproduced with permission from Ref. [110].

4. Iridium(III) complexes for anion sensing

The iridium(III) polypyridyl complexes have been less explored as chemosensors for anions than the rhenium(I) and ruthenium(II) polypyridyl complexes. The early reports of iridium(III) polypyridyl complexes in chemosensors were mainly limited to recognizing oxygen and cations [40, 57]. Up to now, only a few examples of iridium(III) complexes have been reported to recognize anions [60,112-114].

4.1 Thiourea-based Ir(III) complexes as chemosensors

Lo and co-workers reported the synthesis and properties of a series of luminescent cyclometalated iridium(III) polypyridinethiourea complexes **38-40** [112]. These complexes showed luminescence quenching upon addition of acetate, fluoride and dihydrogen phosphate ions. The binding stoichiometries were determined to be 1:1 in all cases. Fig.8 showed a type 1:1 titration curve for luminescence intensity upon addition of OAc^- to a CH_3CN solution of complex **40c**. The $\log K_s$ values for the binding of OAc^- range from 4.03 to 4.35 and are larger than those for F^- (from 3.13 to 3.73) and H_2PO_4^- (from 3.12 to 3.68). The affinity of these complexes for OAc^- is stronger than that for F^- and H_2PO_4^- , which is attributed to a combined effect of the basicity and molecular geometry of the anions.

Fig. 8. Luminescence spectral traces of complex **40c** (120 μ M) in CH_3CN (0.1 M TBAP) upon addition of OAc^- at 298 K. Reproduced with permission from Ref. [112].

4.2 Imidazole-based Ir(III) complexes as chemosensors

A series of cationic Ir(III) complexes **41-43** containing the iridium(III) polypyridine moiety as a chromophore and the polarized N–H proton of imidazolyl substituent as an anionic recognition site have been synthesized and investigated by Huang and co-workers [113]. The UV-vis absorption and emission spectra of these complexes showed significant changes upon addition of F^- , OAc^- , and H_2PO_4^- . The solution colors of the complexes changed from yellow-green to brown, which can be detected by the naked eye. Moreover, the emission intensity of these complexes displayed strongly quenching, which was attributed to the photoinduced electron transfer process from the electron lone pair on the imidazolyl group after the deprotonation of the N–H proton quenched the emission of the complex.

5. Concluding remarks

We have illustrated in this review that different types of ruthenium(II), rhenium(I) and iridium(III) polypyridyl complexes with polarized N–H recognition motifs as recognition motifs can be designed and synthesized as anion receptors. In particular, both selectivity and sensitivity for different anions is greatly enhanced upon coordination of the organic ligand bearing suitable functional groups for anion recognition to transition metals. The incorporation of potential luminescent chromophores into the structure provides a very sensitive way to detect the presence of the anions. The degrees of probe–anion interactions can be easily visualized via naked eye colorimetric or luminescent responses.

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