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Detection of Bio-Relevant Metal Ions by Luminescent Ru(II)-Polypyridyl Based Sensors

Pramod Kumar and Sushil Kumar

Abstract

Biorelevant metal ions such as Cu^{2+} and $\text{Fe}^{2+}/\text{Fe}^{3+}$ participate in various biological events which include electron transfer reactions, delivery and uptake of oxygen, DNA and RNA syntheses, and enzymatic catalysis to maintain fundamental physiological processes in living organisms. So far, several analytical techniques have been investigated for their precise detection; however, luminescence-based sensing is often superior due to its high sensitivity, selectivity, fast and easy operation and convenient cellular imaging. Owing to their immense photophysical and photochemical properties stemming from large Stokes shift, absorption in visible region, good photostability and long excited state lifetimes, Ru(II)-polypyridyl-based complexes have gained increasing interest as luminophores. Over past few decades, several Ru(II)-polypyridyl based chemosensors have rapidly been developed for detection of different biorelevant and other metal ions. The main object of this book chapter is to cover a majority of Ru(II)-polypyridyl based chemosensors showing a selective and sensitive detection of bio-relevant Cu^{2+} and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions. The photophysical properties of Ru(II) complexes, detection of metal ions, sensing mechanism and applications of these sensors are discussed at a length.

Keywords: Ru(II)-polypyridyl, phosphorescence, sensing, biorelevant, metal ions

1. Introduction

The aim of this chapter is to familiarize readers about the luminescent sensing applications of Ru(II)-polypyridyl fragment based chemical systems for the detection of bio-relevant metal ions. Biorelevant metal ions such as Cu^{2+} and $\text{Fe}^{2+}/\text{Fe}^{3+}$ participate in various biological events which include electron transfer reactions, delivery and uptake of oxygen, DNA and RNA syntheses and enzymatic catalysis [1, 2]. Ru(II)-polypyridyl complexes have been considered as ideal phosphorescent chemosensors due to their distinguished photochemical and photophysical properties such as absorption in visible region, emission in long wavelength red and near-infrared regions, long lifetimes of excited state, redox- and photo-stability [3]. The UV-visible spectrum of this system displays several interesting features such as ligand centered ($\pi \rightarrow \pi^*$) transitions at high energy (185–285 nm), two weak signals between 322–344 nm, and most intense peak near λ_{max} 450 nm which is attributed to the MLCT (metal to ligand charge transfer) transition [4, 5]. The Ru(II)-polypyridyl centre worked as excited state redox active agent in electron transfer

processes, and showed very good emission properties [4, 5]. Ru(II)-polypyridyl complexes are classical luminophores showing excitation at 450–470 nm and wide emission bands centred at 600–620 nm. In general, three bidentate (bipyridine/phenanthroline) or two tridentate (terpyridine) ligands have been employed to prepare Ru(II)-polypyridyl chemosensors which exhibit outstanding optical and electrochemical properties. The focus of this chapter is to illustrate the chemical versatility of such chelating systems and their utilization in the detection of different analytes. Over the past few decades, the investigation into the salient properties of ruthenium (II)-polypyridyl complexes has turned out to be a major research area which stems especially from their appealing photochemical and photophysical properties [6, 7]. The next few sections have collected selected examples where an appropriate category of receptors based on Ru(II)-polypyridyl fragment has been selected for showcasing a particular theme.

2. Ru(II)-polypyridyl linked terpyridine chelate based sensors

Terpyridine (terpy) and its derivatives are the most frequently employed N-heterocyclic chelating agents which exhibit an exceptional binding ability for various metal ions. The typical cation binding area of terpy unit contains three nearly coplanar N atoms and its complexes have widely been used as signaling units at molecular and supramolecular levels.

In 2013, Wang and group developed [8] a Ru(II)-polypyridyl based luminescent sensor **1** containing a terminal terpyridine (terpy) moiety for Fe^{2+} ions recognition (**Figure 1**). The fluorescence emission studies of probe **1** were investigated in acetonitrile: HEPES buffer solution (1/71, v/v) of pH 7.2. Luminescence based titration of Fe^{2+} (0.5 equiv) with sensor **1** in acetonitrile solution clearly displayed a visible color change (light yellow to red-purple) with concomitant changes in emission and absorption spectra of probe **1**. The emission of probe **1** was quenched at 608 nm upon successive addition of Fe^{2+} ions in aqueous CH_3CN solution. Probe **1** has exhibited excellent selectivity towards Fe^{2+} ions with a detection limit of 4.58×10^{-8} M and also served as a good colorimetric sensor for Fe^{2+} ion among other metal ions. A 2: 1 binding stoichiometry of Fe^{2+} with complex **1** has been found in accordance with the coordination of terminal terpy units with Fe^{2+} ion and formation of 1-Fe^{2+} was confirmed by spectroscopic methods (**Figure 1**).

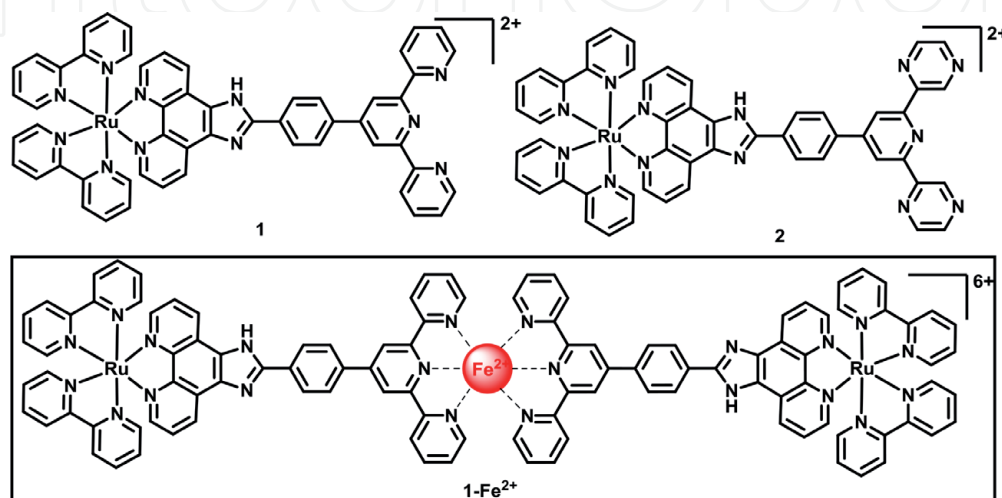


Figure 1.
Chemical drawing of probes **1–2** and proposed binding of 1-Fe^{2+} .

The same group reported [9] another Ru(II)-polypyridyl based probe **2** bearing a dipyrazinylpyridine moiety in 2015 which exhibited a sensitive a selective detection for Cu^{2+} ion in presence of other metal ions (**Figure 1**). The UV-visible and emission spectral changes clearly revealed the coordination of Cu^{2+} ion with the neutral N donors of dipyrazinyl-pyridine moiety of sensor **2**. A significant quenching (upto 97%) in the luminescence intensity of probe **2** at 607 nm has been observed when 2.0 equiv. of Cu(II) ions were added to a CH_3CN /HEPES buffer solution of probe **2**. The detection limit and association constant have been calculated as 2.73×10^{-6} M and $1.88 \times 10^4 \text{ M}^{-1}$ respectively, with a 1:1 binding stoichiometric ratio for complex **2**- Cu^{2+} . The luminescence of probe **2** was almost regenerated when a solution of complex **2**- Cu^{2+} was treated with excess EDTA. Probe **2** could be used for Cu^{2+} detection by probe in a wide range of pH upto 3.0–7.0 as the luminescence of **2** was independent of pH in this range.

3. Ru(II)-polypyridyl linked DPA chelate based sensors

Because of the strong coordinating affinity of N donor atoms of DPA (bis-(pyridin-2-ylmethyl)amine) unit with Zn^{2+} and Cu^{2+} ion, DPA tethered lumino-phores are gaining increasing interest in this research area. In year 2011, Zhang et al. constructed [10] a luminescent probe **3** having a free terminal dipicolylamine or DPA unit to detect Cu^{2+} ions (**Figure 2**). The emission signal of probe **3** at 612 nm was drastically quenched upon introducing 1.0 equiv. Cu^{2+} into an aqueous solution of probe **3** (10 mM HEPES buffer solution; pH 7.2). Job's plot data analyses displayed the formation of complex **3**- Cu^{2+} with 1:1 stoichiometric ratio (**Figure 2**). Furthermore, non-luminescent complex **3**- Cu^{2+} became emissive in the presence of sulfide ions. In the presence of S^{2-} ions, Cu(II) ion is effectively removed from **3**- Cu^{2+} to form a stable CuS species which ultimately led to a turn-on fluorescence response.

Xianghong et al. reported a Ru(II)-based probe **4** containing two DPA units as receptors for Cu^{2+} ions (**Figure 2**) [11]. The absorption and emission spectral changes observed after Cu^{2+} addition with **4** clearly indicated the coordination of Cu^{2+} with DPA moieties of complex **4**. The luminescence intensity of probe **4** at 630 nm was quenched upto a significant extent when Cu^{2+} was successively added in ethanol solution of probe **4**. Job's plot analyses revealed the formation of **4**- Cu^{2+} with 1: 2 ratio which has also been corroborated with mass spectral data. Probe **4** exhibited a selective detection of Cu(II) over other cations with a binding constant

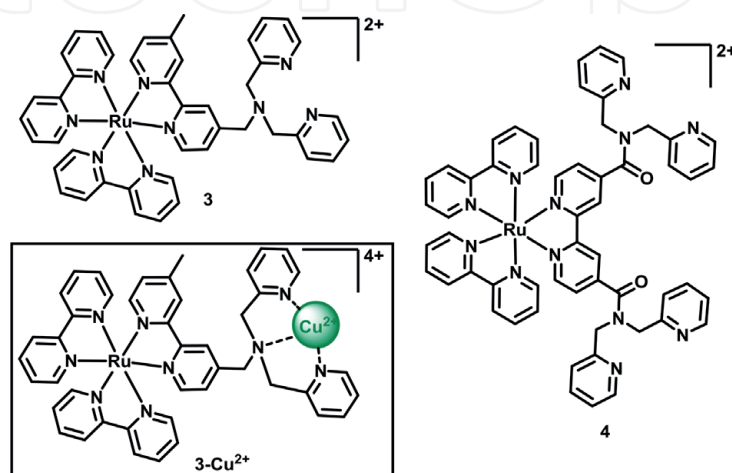
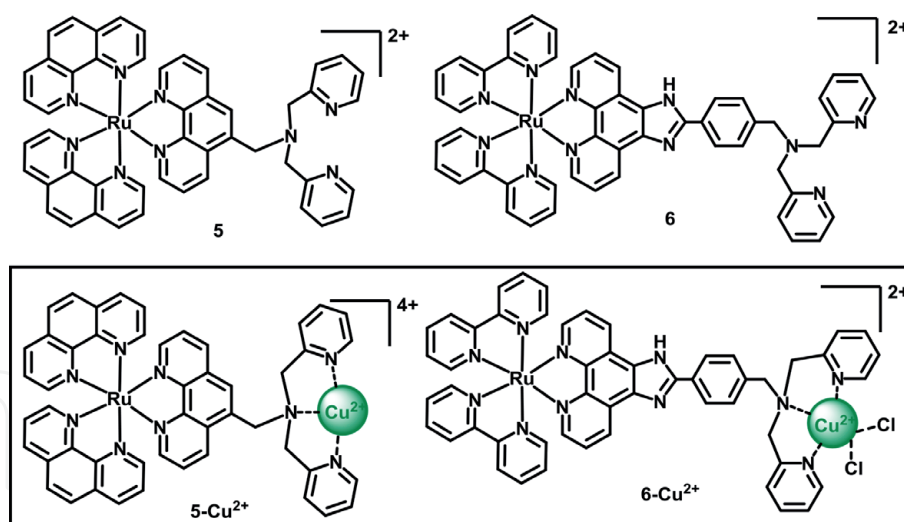


Figure 2.
 Chemical drawing of probes **3–4** with proposed binding of **3**- Cu^{2+} .

**Figure 3.**

Chemical drawing of probes 5–6 with their proposed binding to Cu²⁺ ions.

value of $5.89 \times 10^4 \text{ M}^{-1}$. The selective recognition of Cu(II) has been attributed to the high thermodynamic affinity of this metal ion towards N and O coordinating sites.

Liu et al. designed [12] a DPA tethered Ru(II) luminophore (5) which serves as an excellent luminescent probe for Cu²⁺ ion detection in pure water (**Figure 3**). The luminescence emission of probe 5 has been selectively quenched in the presence of Cu²⁺ among various other cations. An appreciable water solubility and usage in wide pH range make probe 5 a potential candidate for practical applications. The LOD value of 5 for Cu²⁺ has been calculated as $1.55 \times 10^{-7} \text{ M}$. The DPA chelate of probe 5 coordinated to the copper centre through N₃ atoms and form a non-luminescent 5-Cu²⁺ complex.

Recently, an imidazo-phenanthroline linked Ru(II) complex 6 with DPA as terminal binding site has been reported by Arora et al. (**Figure 3**) [13]. Probe 6 serves as selective and phosphorescent sensor for recognition of Cu²⁺ metal ion in aqueous medium. The addition of Cu²⁺ to probe 6 leads to coordination, as evidenced from the adequate quenching in emission signal of probe 6 at 615 nm. Probe 6 also acted as a colorimetric sensor towards Cu²⁺ ions in aqueous solution as the red-orange color of 6 was turned to light yellow (visible to naked eyes) upon adding Cu²⁺ ions to it. The Job's plot data, LOD (1.89 M) and association constant ($1.14 \times 10^5 \text{ M}^{-1}$) values exhibited a 1: 1 complex formation of Cu²⁺ with probe 6. Copper(II) selectivity of 6 is barely affected in the presence of other metal ions and biological targets such as amino acids and glucose. The emission of probe 6 was recovered when a sodium salt of EDTA was added to the non-luminescent complex 6-Cu²⁺.

4. Ru(II)-polypyridyl linked macrocyclic chelate based sensors

Macrocycles are particularly attractive classes of compound in different research areas because of their relative ease of functionalization and the availability of a central cavity with different conformations and sizes. Depending on the size of their macrocyclic crown, these compounds exhibit strong binding to various alkali and/or transition metal ions. A number of macrocyclic compounds have found applications and uses in sensing and other fields.

Paul et al. developed [14] a luminescent probe 7 containing a macrocyclic receptor for detection of Cu²⁺ ion in acetonitrile solution (**Figure 4**). Probe 7 displayed a typical UV–visible spectrum with absorption maxima at 453 nm (attributed to

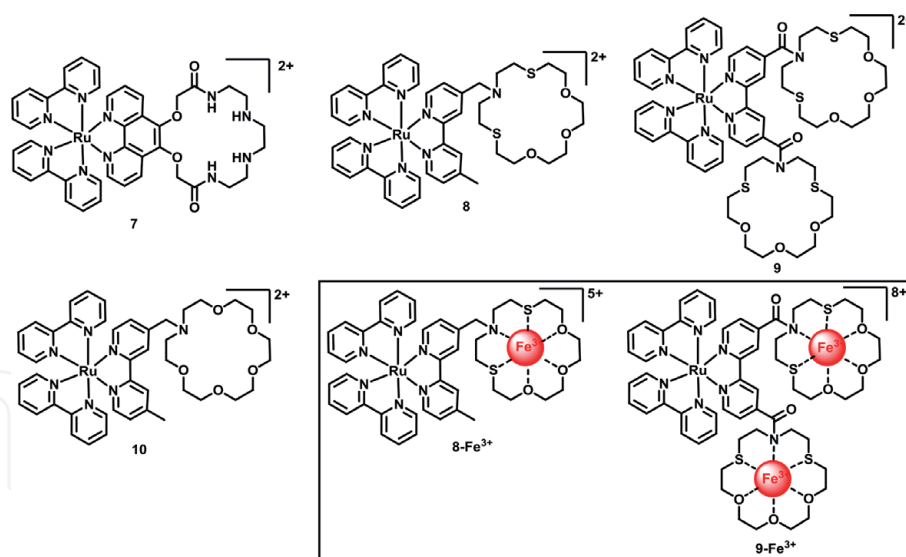


Figure 4.
Chemical drawing of probes 7–10 with their proposed binding to Fe³⁺ ion.

MLCT). Upon excitation at 460 nm, probe 7 exhibited an emission response at 603 nm. Successive addition of Cu²⁺ to CH₃CN solution of 7 resulted in a significant quenching of emission intensity. A strong affinity of coordinating sites (N and O donor atoms) available in receptor unit towards Cu²⁺ ion is favorable for appreciable binding.

Two novel Ru(II)-based fluorescent probes 8 and 9 having terminal NS₂O₃ macrocyclic rings as metal ion receptor were reported by Boricha et al. in 2012 (**Figure 4**) [15]. Probes 8 and 9 exhibited the characteristic absorption bands near 454 nm due to a MLCT transition and an emission signal in the range of 602–632 nm in acetonitrile solution. Addition of Cu²⁺ to probe 8 leads to the binding as evidenced by 87% luminescence quenching in emission intensity. On the other hand, addition of Fe³⁺ yielded a quenching in emission signal of probe 8 upto 96%. Probes 8 and 9 also displayed strong interactions with soft metal ions such as Pb²⁺ and Hg²⁺ ions. The presence of S atoms in the macrocyclic rings facilitated the affinity of these sensors towards soft acids. Probes 8 and 9 showed highest selectivity with Fe³⁺ ion and form hexa-coordinated complexes 8-Fe³⁺ and 9-Fe³⁺.

For comparison, another structurally similar probe 10 containing a macrocyclic ring with NO₅ donors has also been developed (**Figure 4**) [15]. Interestingly, probe 10 served as a highly selective sensor for the detection of only Cu²⁺ ions over other metal ions, and a binding constant of $9.51 \times 10^2 \text{ M}^{-1}$ has been reported in this case. Replacement of soft donor S atoms with hard donor N atoms in the macrocyclic ring resulted with the selectivity enhancement of probes.

Due to their strong binding affinity towards metal ions and appreciable water solubility, cyclen (1, 4, 7, 10-tetraazacyclododecane) based derivatives have gained huge attraction in the research areas of chemistry and biology. The metal ion binding with cyclen unit induces a perturbation in electronic structure which results in the change of photophysical properties of luminophores.

A cyclen tethered luminescent probe 11 has been designed and synthesized by Li and group [16] for Cu²⁺ ion detection in pure water (**Figure 5**). Probe 11 exhibited classical UV-visible and emission spectra with absorption maxima at 450 nm and emission maxima at 604 nm. Upon addition of 1.0 equiv. of Cu²⁺ ions, the emission intensity was quenched to significant amount. Interaction between probe 11 and Cu²⁺ were believed to entail 1: 1 complex formation which is consistent with the availability of only one receptor per luminescent probe. Probe 11 was found suitable for Cu²⁺ detection in pH range of 5–11, and the binding constant value was

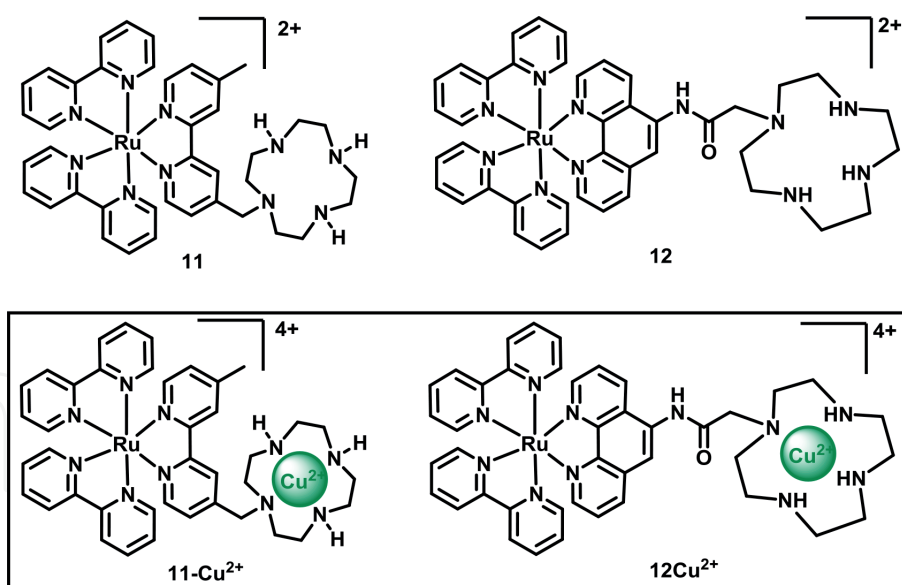


Figure 5.
Chemical drawing of probes **11–12** and their proposed binding to Cu^{2+} ion.

calculated as $2.36 \times 10^4 \text{ M}^{-1}$. The strong Cu binding of **11** has been attributed to high thermodynamic stability and huge formation constant value of ensemble **11-Cu²⁺**. Moreover, probe **11** displayed a off–on–off emissive response with an alternative addition of Cu^{2+} and S^{2-} ions in water.

Ye et al. developed another cyclen unit based fluorescent probe **12** to prepare a complex **12-Cu²⁺** (**Figure 5**) [17]. Non-luminescent complex **12-Cu²⁺** was used to selectively detect sulfide ions under physiological conditions. Upon excited with 450 nm light, probe **12** showed a luminescence response at 605 nm. The red–orange luminescence of probe **12** was significantly quenched with the addition of 10 μM Cu^{2+} ions in HEPES buffer solution. The interaction between **12** and Cu^{2+} are believed to involve 1:1 complex formation as evidenced by Job's plot and mass spectral analyses. The luminescence intensity of **12** has been almost completely recovered by treating H_2S with the non-emissive complex **12-Cu²⁺**.

5. Ru(II)-polypyridyl linked imidazole chelate based sensors

Luminescent Ru(II)-polypyridyl complexes linked with 2-hydroxyphenylimidazo unit are gaining increasing interest in the monitoring and detection of copper ions owing to the strong binding affinity and straight coordination of 2-hydroxyphenylimidazo unit. Zhang et al. constructed [18] a luminescent probe **13** containing 2-hydroxyphenylimidazo moiety which acts as highly selective sensor for Cu^{2+} ion recognition in aqueous media (**Figure 6**). Upon exciting at 467 nm light under physiological conditions, probe **13** displayed an emission spectrum with emission maxima at 585 nm. Probe **13** provides two donor (N, O) sites to link with Cu^{2+} ion to form complex **13-Cu²⁺** in 1:1 binding stoichiometry.

Later, Zheng's group introduced [19] another 2-hydroxyphenylimidazo based luminescent probe **14** for highly selective and effective detection of Cu^{2+} ions in CH_3CN -HEPES buffer solution of pH 7.2 (**Figure 6**). To confirm the Cu^{2+} binding with terminal 2-hydroxyphenylimidazo of **14**, the absorption and emission spectral changes have been observed. Introduction of Cu^{2+} leads to coordinate with receptor, as evidenced by the quenching in the emission intensity of probe **14**. A strong interaction of 2-hydroxyphenylimidazo moiety with Cu(II) (**14-Cu²⁺**) is validated with a binding constant value of $1.09 \times 10^5 \text{ M}^{-1}$.

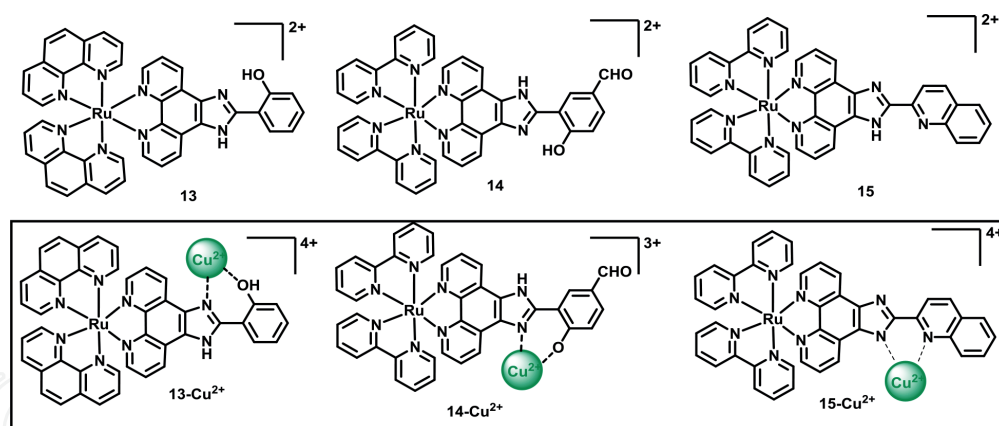


Figure 6.
 Chemical drawing of probes 13–15 and their proposed binding to Cu²⁺ ion.

Recently, a novel quinoline-tethered Ru(II)-based luminescent probe **15** has been developed by Kumar et al. (**Figure 6**) [20]. Probe **15** displayed an absorption maxima at 470 nm and emission intensity at 604 nm. Addition of Cu²⁺ in the solution of probe **15** leads to the binding as evidenced by the measurement of UV–visible and emission spectral changes. A bathochromic shift in absorption wavelength at 470 nm and appearance of new band between 620 nm to 720 nm (Cu based *d-d* transition) indicated the coordination of Cu²⁺ with probe **15**. A large decrease in emission intensity at 604 nm has also been only in the presence of Cu(II), over other cations. The LoD and binding constant values are calculated as 5.07×10^{-8} M and 5.00×10^5 M⁻¹. Interaction of probe **15** with Cu²⁺ is believed to entail 1:1 formation of complex **15-Cu²⁺**.

In a very recent report, Song and group reported [21] a luminescent probe **16** containing a terminal pyrazole fragment connected with Ru(II) luminophore *via* imidazole linker (**Figure 7**). Probe **16** proved to be fast and highly selective fluorescent chemosensor for Cu²⁺ ions in aqueous buffer solution (pH 7.4). The emission intensity of probe **16** at 621 nm (λ_{ex} 460 nm) was adequately quenched upon introducing paramagnetic Cu²⁺ ion with a detection limit of 8.33×10^{-8} M. Depending on the pH of probe's solution, a protonation-deprotonation process of N atoms of imidazole fragment has also been experienced. Job's plot analyses demonstrated the formation of complex **16-Cu²⁺** with a 1:1 binding ratio. The formation of **16-Cu²⁺** was also confirmed by broadening in resonances and disappearance of NH signals in ¹H NMR spectrum of **16** on adding Cu²⁺ ions. The red luminescence of probe **16** was regenerated with addition of an excess of EDTA to complex **16-Cu²⁺**.

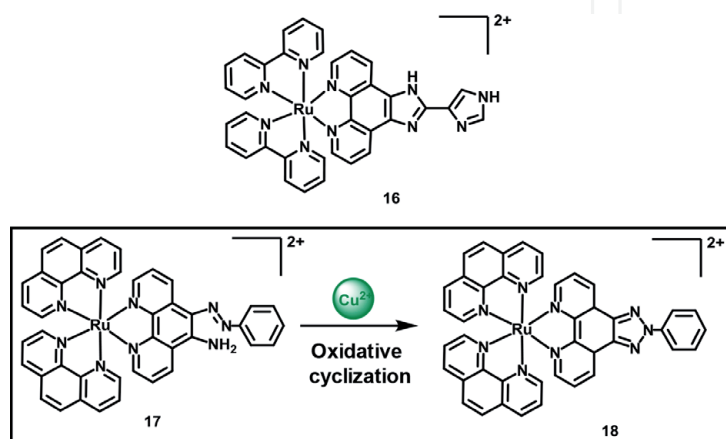


Figure 7.
 Chemical drawing of probes 16–17 and oxidative cyclization of 17 to 18 by Cu²⁺ ion.

In 2015, Zhang et al. described [22] the synthesis of *o*-(phenylazo)aniline based non-luminescent probe **17** for sensing of Cu^{2+} ions with a emissive switch-on response (**Figure 7**). Addition of Cu^{2+} to probe **17** caused the oxidative cyclization of probe **17** to produce a highly luminescent complex **18** containing a benzotriazole fragment. Probe **17** was found completely soluble in water and exhibited an appreciable photostability in presence of light. The cyclization of *o*-(phenylazo)aniline moiety could easily be performed by introducing only 1 equiv. of $\text{Cu}(\text{II})$. Addition of 1 equiv. of Cu resulted with the large increase in luminescence intensity of **18**. The Cu sensing by probe **17** is unique as Cu^{2+} is only participating in cyclization reaction but does not coordinate with the receptor. Probe **17** was found highly selective for Cu^{2+} in the presence of various cations, with a detection limit of 4.42×10^{-9} M. Probe **17** has also been employed to detect Cu^{2+} in live-pea aphids with a switch-on emissive signal.

In 2013, Chao and co-workers reported [23] a dinuclear $\text{Ru}(\text{II})$ -based luminescent probe **19** for sensitive and selective detection of Cu^{2+} ions (**Figure 8**). Upon addition of Cu^{2+} ions (2.0 equiv.) into probe solution, the emission intensity at 600 nm was significantly quenched (96%). A naked eye color change could also be observed under UV light exposure. Binding of Cu with **19** is reported to involve 1:1 complex formation as evidenced by ESI-MS, NMR and EPR measurements, and the detection limit is computed to be 3.33×10^{-8} M. The luminescence of **19**- Cu^{2+} was recovered with an excess addition of EDTA to the mixture of Cu^{2+} and probe **19**. The selectivity studies clearly demonstrated no interference of other cations in sensing of probe **19** towards Cu^{2+} ions.

Cheng et al. developed [24] two dinuclear ruthenium complexes **20** and **21** for the luminescence based recognition of Cu^{2+} ions (**Figure 8**). Investigation of luminescence properties of these probes indicated higher emission response for probe **20** at 609 nm compared to probe **21**. Probe **20** detected Cu^{2+} selectively over other cations, and the luminescence of this probe was almost completely quenched in presence of $\text{Cu}(\text{II})$ ion. Nitrogen atoms from imidazole fragments and oxygen atom of furan participated in coordination to form complex **20**- Cu^{2+} with 1:1 ratio of binding. It is noteworthy that probe **21** displayed an increase in luminescence in various metal ion with no metal ion selectivity. The enhancement in emission intensity of probe **21** is attributed to the disturbance of photoinduced electron transfer process as the lone pair on S donor site becomes unavailable after metal ion coordination.

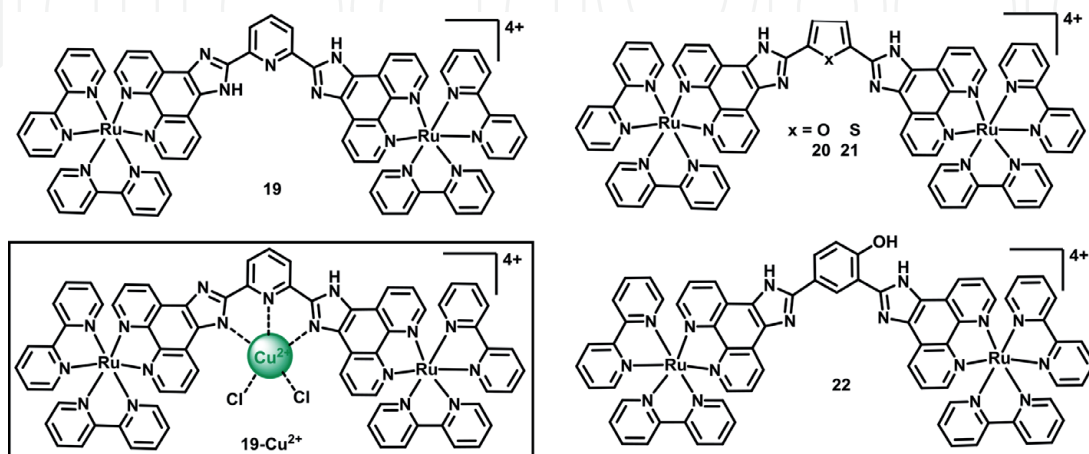


Figure 8.
Chemical drawing of probes **19**–**22** and proposed binding of **19** to Cu^{2+} ion.

Zheng et al. developed [19] a 2-hydroxyphenylimidazo based luminescent probe **22** for Cu(II) ion recognition in aqueous buffer solution (pH 7.2; HEPES) containing 1% acetonitrile (**Figure 8**). To validate the binding of Cu²⁺ with probe **22**, the absorption and emission spectral changes were investigated. Binding of Cu²⁺ with 2-hydroxyphenylimidazo fragment leads to a significant quenching in emission intensity of probe **22**. This probe showed a ON–OFF–ON emissive response with an alternative addition of Cu²⁺ and CN[−] ions. The detection limit and the association constant for Cu ion sensing by **22** were calculated as 3.77×10^{-7} M and 4.31×10^4 M^{−1} respectively.

6. Ru(II)-polypyridyl linked triazole chelate based sensors

In recent years, 1,2,3-triazole based synthetic receptors have been considered to be an excellent motif for recognition of different analytes [25]. As N-atom containing Lewis bases, the triazole-based derivatives display strong metal ion binding properties and have been employed in different areas of research.

Triazole Ramachandran et al. constructed [26] a luminescent probe **23** containing a benzothiazole unit connected to Ru^{II}(bpy)₃ luminophore through a triazole linker (**Figure 9**). The probe was found highly selective towards Cu²⁺ ion detection and the red-orange emission of **23** at 630 nm was quenched upto 80% with addition of Cu²⁺ in HEPES buffer solution of pH 7.4. A 1:1 ratio of Cu binding with **23** has been confirmed with the help of Job's plot and ESI-mass spectral analyses. As evidenced by selectivity studies, other cations hardly affect the sensing ability of probe **23** towards Cu²⁺ ion. The binding constant and limit of detection values were in order of 5.11×10^4 M^{−1} and 7.00×10^{-7} M respectively.

The same group reported a dinuclear Ru^{II}(bpy)₃ based luminescent probe **24** which contain a *p*-tert-butylcalix[4]arene fragment as receptor for Cu²⁺ ions (**Figure 9**) [27]. As indicated by phosphorescence based titration experiments, probe **24** was found effective and selective Cu²⁺ ion sensor with a *turn-off* emission signal at 637 nm. Binding of Cu²⁺ was evidenced by the large decrease in luminescence intensity of probe **24**. The strong interaction of calixarene based receptor with Cu²⁺ is believed to involve 1:1 formation of **24**-Cu²⁺ with a binding constant value of order 2.31×10^4 M^{−1}. The red-orange luminescence of **24** was revived when S^{2−} ions were added to complex **24**-Cu²⁺. Due to a very low cytotoxicity of probes **23** and **24**, cell imaging experiments have also been performed using these probes in human lung cancer A549 and MCF-7 cell lines.

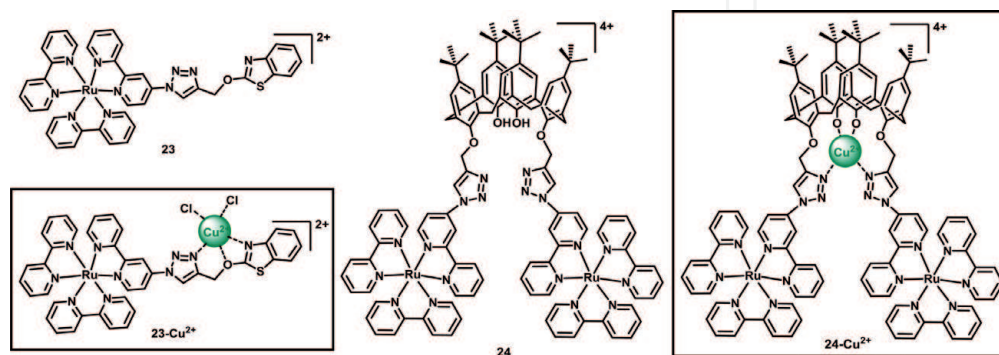


Figure 9.
 Chemical drawing of probes **23–24** and their proposed binding to Cu²⁺ ions.

7. Ru(II)-polypyridyl linked carboxamide chelate based sensors

The coordination behavior of carboxamide group with different transition metal ions has extensively been investigated and well documented in the literature. The rapid growth in the development of carboxamide based organic and inorganic synthetic receptors is due to the realization of their important roles in chemistry, catalysis, medicine and the biology. In the present section, we have highlighted few luminescent sensors containing carboxamide group in the framework of metal ion receptors.

A series of luminescent Ru(II)-polypyridyl based sensors **25–27** have been designed for efficient sensing of Cu^{2+} ions. Sensors **25–27** show a MLCT absorption band at 450 nm and emission band at 620 nm after excitation this MLCT band. (**Figure 10**) [28]. Two equivalents of Cu^{2+} ion was enough to quench the emission of **25–27** completely. To selectivity of **25** towards Cu^{2+} ion in presence of other metal ions was studied in different pH and found the best selectivity and quenching at pH 5 only.

Another carboxamide linked Ru(II)-polypyridyl based sensor **28**, was developed [29] by Gopidas and co-workers showed unique chemical oxidation properties and Turn-ON emission with Cu^{2+} ion in CH_3CN (**Figure 10**). The emission intensity at 620 nm of **28** quenched by unique and fast electron transfer from the phenothiazine moiety to the Ru^{2+} core. Interestingly, the luminescence intensity of **28** enhanced by Cu^{2+} ion due to the oxidation of phenothiazine moiety Cu^{2+} ion. In presence of Cu^{2+} ion, phenothiazine is unable for emission quenching of Ru^{2+} centre.

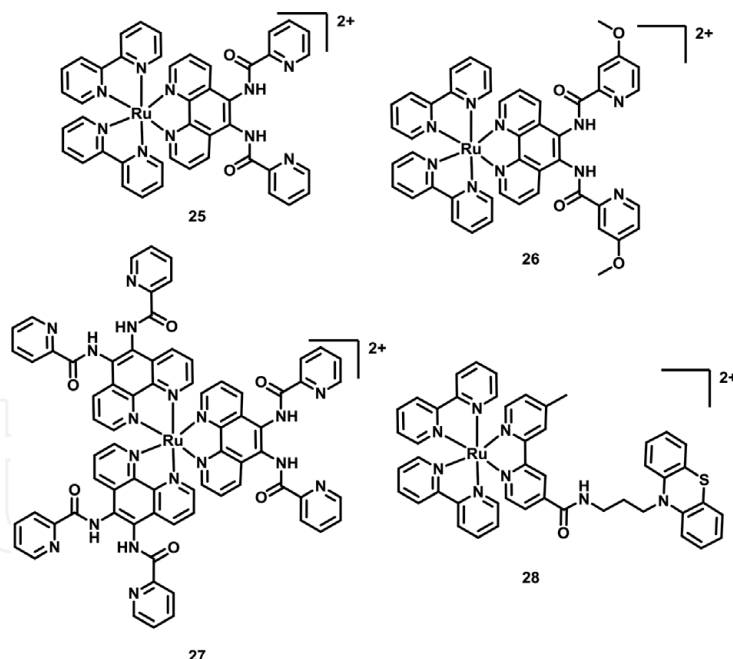


Figure 10.
Chemical drawing of probes **25–28**.

8. Ru(II)-polypyridyl linked imine chelate based sensors

Imine base ligands (Schiff bases) play important role in coordination chemistry due to their easy synthesis, high stability and insensitive properties towards air and moisture. Moreover, the electronic and steric features of these imine based ligands could easily be tuned by varying appropriate condensing partners.

These ligands bind through imine-N atom and display adequate structural flexibility and strong binding ability for various cations. Over the past decades, imine based derivatives are gaining increasing interest in the research area of electrochemical and optical sensing. In the present section, we have discussed luminescent Ru(II)-polypyridyl sensors containing an imine group in the metal ion binding site.

Kumar et al. described [30] a luminescent probe **29** containing a terminal thiophene unit linked with Ru(II)-polypyridyl based luminophore *via* imine bond (**Figure 11**). The water soluble probe having imine-N and thiophene-S coordinating sites detected Fe^{3+} ions through turn-off luminescence response at 615 nm, over other metal ions. However, a minor change in intensity has also been observed in the presence Cu^{2+} and Ag^+ ions. A 1: 1 stoichiometry of complex **29**- Fe^{3+} was validated by Job's plot data and mass spectroscopic studies. The detection limit (LoD) and the binding constant for Fe^{3+} ion were computed as 0.11 ppm and $1.57 \times 10^3 \text{ M}^{-1}$ respectively. Moreover, the red-orange luminescence of probe **29** was restored with the addition of EDTA to a buffer solution of complex **29**- Fe^{3+} . For practical applications on real samples, probe **29** has been investigated for paper strips, polystyrene films and live cell imaging experiments.

Zhang et al. reported [31] the formation of luminescent probe **30** which displays a switch-off emission response in presence of Cu^{2+} ions in aqueous medium (**Figure 11**). Probe **30** detects Cu^{2+} selectively over various other metal ions, except a marginal quenching observed in case of Zn^{2+} ions. Binding of Cu^{2+} with **30** was evidenced by a red shift observed in absorption wavelength and a significant decrease in emission intensity. The luminescence of probe **30** was revived by treatment of non-luminescent complex **30**- Cu^{2+} with L-histidine. A limit of detection of order $3.50 \times 10^{-10} \text{ M}$ and an association constant value of $4.44 \times 10^3 \text{ M}^{-1}$ were measured. The effect of pH on sensing ability of probe **30** has been established in this report. The resultant data from pH studies revealed that the most significant quenching occurs in mild basic conditions. The deprotonation of phenolic-OH in basic medium increases its coordinating ability to form non-luminescent complex **30**- Cu^{2+} . Applications of probe **30** were investigated for imaging Cu^{2+} ions in live cells and real water samples.

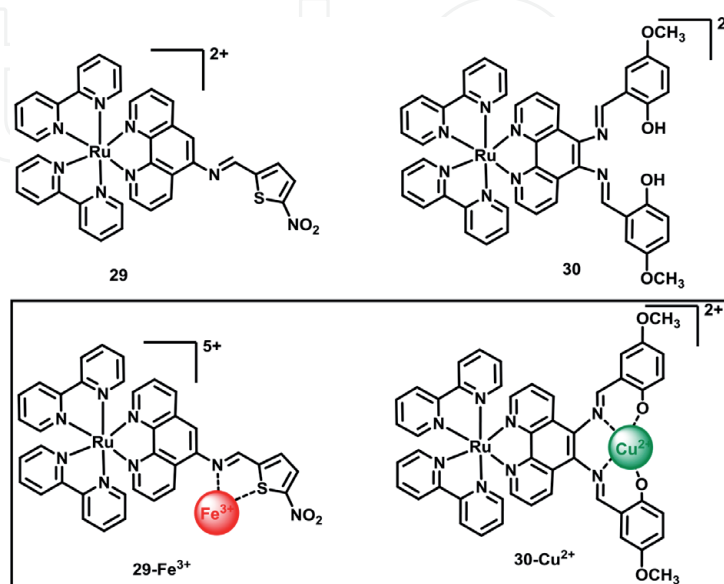


Figure 11.
 Chemical drawing of probes **29–30** and proposed binding of complexes **29**- Fe^{3+} /**30**- Cu^{2+} .

9. Conclusions

The present chapter covers a majority of luminescent Ru(II)-polypyridyl based chemosensors for the selective recognition of biorelevant metal ions such as Cu^{2+} and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions. The sensing behavior of different chemosensors varying from mono- to di-nuclear Ru(II)-polypyridyl complexes has been considered and discussed at a length. The applications encompass many fields including environmental, biological, analytical and medicinal domains. This field of luminescence sensing is quite prosperous and still emerging. Taking advantage of already known ligands topology exploiting their selective binding properties towards a particular metal ion, several chemosensors are developed. The design, detection, mechanisms and applications for different sensors presented in this chapter create huge opportunities for the development of future chemosensors.

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Conflict of interest

Authors have no conflict of interest.

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