Application of Schiff base as a fluorescence sensor

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Abstract

Schiff bases are obtained from condensation of primary amines with carbonyl compounds. There are several applications of Schiff bases which include not only antimicrobial or antifungal activity but also in chemosensor for detection of metal ions. In this review article the applications of Schiff bases in fluorescence sensor are summarized.

Keywords: Schiff base, fluorescence and sensor

INTRODUCTION

A Schiff base which is also known as imine or azomethine is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group has been replaced by an imine or azomethine group. Schiff bases are obtained from condensation of primary amines with carbonyl compounds. There are several applications of Schiff bases (S. Kumar, Dhar, & Saxena, 2009) which include not only antimicrobial or antifungal activity but also in chemical sensor for detection of metal ions.

Schiff base moieties play vital role as a fluorescence sensors due to their ability to form coordination complexes with metal ions (Cozzi, 2004). The development of a chemosensor, which is useful in detection of a metal ion, is important application in biological industry and environmental processes. The fluorescent method has become more popular due to its operational simplicity, high sensitivity and selectivity, naked eye detection moreover it has potential use in medicinal and environmental research (De Silva, et al., 1997).

Fluorescence sensors have been successfully used for the determination of different metal ions, such as, barium, calcium (Kawakami, et al., 2001), cadmium (Y. Li, et al., 2012), cobalt (Abebe, Eribal, Ramakrishna, & Sinn, 2011), chromium (Wan, Guo, Wang, & Xia, 2010), copper (Xu, Wang, Zhang, Wu, & Liu, 2013), ferric (Lin, Long, Yuan, Cao, & Feng, 2009), mercury (Wu, Ma, Wei, Hou, & Zhu, 2013), potassium (Zhou, et al., 2011), lithium (Gunnaugsson, Bichell, & Nolan, 2002), magnesium (Singh, Kaur, Mulrooney, & Callan, 2008), neodymium (Khorasani-Motlagh, Noroozifar, & Mirkazehi-Rigi, 2011), nickel (Ghosh, Chakrabarty, & Mukherjee, 2008), zinc (G-Q. Zhang, Yang, Zhu, Chen, & Ma, 2006) and aluminum (Jia, Cao, Zheng, & Jin, 2013; Kim, et al., 2012; Liao, Yang, Li, Wang, & Zhou, 2013). This paper reviews the applications of Schiff base as a sensor for detection of metal ions.

Schiff base as a fluorescence sensor

Some Schiff base metal complexes show the characteristic luminescence emissions of the central metal ions attributed to efficient energy transfer from the ligand to the central metal ion. Aazam et al. (Aazam, Huseiney, & Al-Amri, 2012) have synthesized mononuclear metal (II) complexes of Zn, Cd, Cu, Ni and Pd with Schiff-base ligand derived from 8-acetyl-7-hydroxycoumarin and P-phenylenediamine. The Schiff base exhibited photoluminescence derived from intraligand (π→π*) transitions. Metal-mediated enhancement is observed on complexation of ligand with Zn and Cd, whereas metal-mediated fluorescence quenching occurs in Cu, Ni and Pd. Similarly, Taha et al. (Taha, Ajlouni, Al-Hassan, Hijazi, & Faiq, 2013) have synthesized complexes of lanthanide (III) (Nd, Dy, Sm, Pr, Gd, Tb, La and Er) with the Schiff base derived from Salicylaldehyde and 1,3-propyldiamine. Sm, Tb and Dy complexes exhibit the characteristic luminescence emissions of the central metal ions associate to energy transfer from the ligand to the metal. Whereas Zhang et al. (J. Zhang, et al., 2012) have synthesized the Schiff base ligands using substituted 2-
hydroxybenzaldehydes with diamines. Using selected complexes as phosphorescent emitting materials, yellow light-emitting devices were fabricated with improved efficiency as compared with the previously reported analogues. In addition, the phosphorescent white organic light-emitting device was fabricated using a single emissive layer composed of yellow- and blue-emitting materials. A series of symmetrical and asymmetric phosphorescent platinum (II) Schiff base complexes with good thermal stability was developed.

Some authors have reported Schiff base type sensors for two metal ions. Ganguly et al. (Ganguly, Paul, Ghosh, Kar, & Guchhait, 2013) have prepared a Schiff base compound 2-((benzylimino)-methyl)-naphthalen-1-ol. Fluorescence yield of the compound has been rationalized in connection with photoinduced electron transfer from the imine receptor to the naphthalene fluorophore unit. Subsequently, an evaluation of the transition metal ion-induced modification of the fluorophore–receptor communication reveals a promising prospect for this compound to function as a fluorosensor for Cu$^{2+}$ and Zn$^{2+}$ ions selectively, through remarkable fluorescence enhancement. Bhorge et al. (Bhorge, et al., 2014) have prepared a new receptor for the detection of Cu$^{2+}$ and Fe$^{3+}$ in solutions as a colorimetric and fluorescent sensor, respectively. This receptor shows highly selective and sensitive recognition toward Cu$^{2+}$ and Fe$^{3+}$ by naked eye UV–Vis and fluorescent color changes in aqueous solution, respectively. The selectivity toward Cu$^{2+}$ or Fe$^{3+}$ was not interfered with by the presence of different other metal ions. This receptor can be used for semi-quantitative recognition of Cu$^{2+}$ ions at ppm level and has potential use in biological cell imaging studies.

Recently, Hsu and Chen (Hsu & Chen, 2018) have prepared Schiff base by reaction of 5-bromo-2-hydroxybenzaldehyde with 2,7-bis (4,4,5, 5-tetramethyl-1,3,2-dioxaborolan-2-yl) pyrene. Pyrene Schiff base sensor exhibits an “off-on-type” mode with high selectivity to Zn$^{2+}$ and Al$^{3+}$ in ethanol (470 nm) and in dimethyl sulfoxide (458 nm) respectively. Tyagi et al. (Tyagi, et al., 2017) have synthesized two novel Schiff base ligands by condensation reaction of amine derivative of 1,2,4-triazole moiety with 2-hydroxy-4-methoxybenzaldehyde and its Co, Ni, Cu and Zn metal (II) complexes. Fluorescence quenching mechanism of metal complexes shows that Zn$^{2+}$ and Cu$^{2+}$ complex binds more strongly to Bovine serum albumin.

Pyrene based thiol containing Schiff base derivative was synthesized (Shellaiah, Rajan, Balu, & Murugan, 2015) via one-pot reaction and utilized as Hg$^{2+}$ ‘turn-on’ sensor. In another study, Shellaiah et al. (Shellaiah, Wu, Singh, Raju, & Lin, 2013) have prepared novel pyrene- and anthracene-based Schiff base derivatives and utilized as fluorescence ‘turn-on’ sensors towards Cu$^{2+}$ and Fe$^{3+}$ ions, respectively, and for aggregation induced emissions. Similarly, as shown in table 1 several studies on Schiff base type sensors for detection of metal ions in presence of other metal ions are listed.

### Table 1: Schiff base sensor for selective detection of metal ions

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Type / derivative of Schiff base</th>
<th>In presence of other metal ions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>Rhodamine-Coumarin</td>
<td>Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Al$^{3+}$, Mn$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Fe$^{3+}$, Fe$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Ag$^+$, Hg$^{2+}$</td>
<td>(An, Yang, Yan, &amp; Li, 2013)</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>2-naphthol</td>
<td>Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Ag$^+$; and other lanthanide</td>
<td>(Hosseini, et al., 2009)</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>(N,N’-bis-(salicylidene)-O-phenylenediamine)</td>
<td>Ca$^{2+}$, Cr$^{3+}$, Al$^{3+}$, Fe$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$</td>
<td>(Harirahan &amp; Anthony, 2014)</td>
</tr>
<tr>
<td>Fe$^{2+}$ &amp; Fe$^{3+}$</td>
<td>2,3-dihydroxybenzaldehyde moiety</td>
<td>Na$^+$, K$^+$, Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Mg$^{2+}$, Ca$^{2+}$</td>
<td>(You, Park, Lee, Ryu, &amp; Kim, 2015)</td>
</tr>
</tbody>
</table>

### Detection of aluminum ion

Gupta et al. (Gupta, Singh, & Kumawat, 2014a) have synthesized Schiff base by condensation of salicylaldehyde and 2-amino-4-phenylthiazole. The interaction of Schiff bases with different metal ions has been studied wherein the results indicated that Schiff base exhibited fluorescent behavior with Al$^{3+}$ ions in methanol with 5.0–13.5 pH range, which could be directly detected by the naked-eye under the UV-lamp.
More than 50-fold enhancement of the fluorescence intensity was observed with Al$^{3+}$ ions and could be measured at 10$^{-7}$ M level by the proposed sensor.

Similarly, Rhodamine functionalized Schiff base was synthesized and its colorimetric and fluorescence responses toward various metal ions were explored (Gupta, Mergu, Kumawat, & Singh, 2015). This rhodamine-derived fluorescent chemosensor exhibited highly selective and sensitive colorimetric and “off–on” fluorescence response towards Al$^{3+}$ in the presence of other competing metal ions. Moreover, Kumar et al. (J. Kumar, Sarma, Phukan, & Das, 2015) have synthesized Schiff base by condensation of 1-Naphthylamine and Benzaldehyde. The Schiff base acts as an effective fluorescent sensor for Al$^{3+}$ by “off-on” mode and 42 times enhancement in fluorescent intensity is observed.

A reversible fluorescent-colorimetric imino-pyridyl bis-Schiff base sensor was also developed (Ghorai, Mondal, Chandra, & Patra, 2015) wherein they have synthesized Schiff base by condensation of p-phenylenediamine & pyridine-4-carboxaldehyde. This Schiff base exhibits an excellent selective fluorescent colorimetric response toward Al$^{3+}$. Shen et al. (Shen et al., 2018) synthesized and characterized Al$^{3+}$ selective fluorescence probe based on naphthalimide-Schiff base useful for practical application to different water samples. Recently, Tian et al. (Tian, et al., 2019) reported a highly selective and sensitive Schiff base (2-hydroxynaphthalene) type fluorescent, which can recognize aluminum ions and exhibit an “off-on” mode with high selectivity.

**Detection of copper ion**

Yang and Qin (H.-G. Li, Yang, & Qin, 2009) designed and synthesized a Schiff base type chemosensor 1-phenyl-3-methyl-5-hydroxyprazole-4-carbaldehyde (benzoyl) hydrazone for Cu$^{2+}$ ion. Fluorescence quenching only for Cu$^{2+}$ demonstrated the high selectivity compared with other metal ions. Köse et al. (Köse, et al., 2015) have prepared Schiff base by reaction of benzaldehyde derivatives with 1,5-diamino naphthalene. They have investigated the electrochemical and photoluminescence properties of the Schiff bases in the different conditions. The sensor properties of the Schiff bases were examined and color changes were observed upon addition of the metal (II) ions of Hg, Cu, Co and Al (III). The Schiff base compounds showed higher selectivity against to the Cu$^{2+}$ ion.

**Detection of other metal ions**

Li et al. (S.-H. Li, et al., 2009) was synthesized Schiff base by condensation of 2, 4-dihydroxynbenzaldehyde with 2-aminobenzeneboronic acid wherein, fluorescence quenching induced by Hg$^{2+}$ rather than other metals. Under the test conditions, an approximately 13-fold increase in the relative fluorescence quantum yield was observed.

A novel sensor, 7-Hydroxy-4-methylcoumarin-8-carbaldehyde-(rhodamine) hydrazone have synthesized (An, et al., 2013) and investigated as a fluorescence chemo sensor for Ca$^{2+}$ in acetonitrile. The compound was found preferential binding to Ca$^{2+}$ ions in presence of excess of other competitive ions with associated changes in its optical and fluorescence spectral behavior.

Hariharan and Anthony (Hariharan & Anthony, 2014) have synthesized different Schiff bases by using different diamines with substituted benzaldehyde. The fluorescence responses of chemo sensor for various metal (II) ions have been studied in dimethylformamide, dimethyl sulfoxide, acetonitrile, methanol and tetrahydrofuran. Practical applications of the chemosensor for selective sensing of Mg$^{2+}$ in different samples from pond, tap, river and ground water have also been demonstrated.

Gupta et al. (Gupta, Singh, & Kumawat, 2014b) have prepared Schiff base by condensation of 4-aminoantipyrine & 4-Hydroxy-3-methoxybenzaldehyde. The complexation behavior of chemo sensor with different metal ions including Zn$^{2+}$ ions in methanolic solution was studied on UV–vis absorption spectra and Photo fluorescent spectra. Results showed that the chemo sensor exhibited 55-fold enhancements in fluorescence at 533 nm after adding Zn$^{2+}$ ions. The chemo sensor showed excellent selectivity for fluorescent behavior in acidic pH range.

Pan et al. (Pan, et al., 2017) have prepared Schiff base by reaction of 2-Aminophenol & (4-diphenyl amino) benzaldehyde. The chemo sensor shows selective “turn-off” fluorescence response to Fe$^{3+}$.
in living cells. Similar examples of different Schiff bases for detection of metal ions in presence of other metal ions are listed in table 2.

**Table 2: Different Schiff bases as sensors for selective detection of metal ions.**

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Type / derivative of Schiff base</th>
<th>In presence of other metal ions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$^{3+}$</td>
<td>8-hydroxyquinoline-5-carbaldehyde</td>
<td>Ag$^+$, Ca$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Cr$^{3+}$, Cu$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Hg$^{2+}$, K$^+$, Mg$^{2+}$, Mn$^{2+}$, Na$^+$, Ni$^{2+}$, Pb$^{2+}$, Zn$^{2+}$</td>
<td>(Jiang, et al., 2011)</td>
</tr>
<tr>
<td></td>
<td>Derivative of benzohydrazide</td>
<td>Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Mg$^{2+}$, Ca$^{2+}$, Pb$^{2+}$.</td>
<td>(Lee, et al., 2014)</td>
</tr>
<tr>
<td></td>
<td>1-(2-pyridylazo)-2-naphthol</td>
<td>Ba$^{2+}$, Ca$^{2+}$, Cr$^{3+}$, Cs$^+$, Hg$^{2+}$, K$^+$, Li$^+$, Mg$^{2+}$, Na$^+$, and Sr$^{2+}$</td>
<td>(Gupta, Shoora, Kumawat, &amp; Jain, 2015)</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>Pyrene Schiff base</td>
<td>Na$^+$, K$^+$, Ca$^{2+}$, Mn$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Sn$^{2+}$</td>
<td>(Sivaraman, Anand, &amp; Chellappa, 2012)</td>
</tr>
<tr>
<td></td>
<td>1-[(2-naphthalenylimino) methyl]-2-naphthalenol</td>
<td>Fe$^{2+}$, Ag$^+$, Ca$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Cr$^{3+}$, Mg$^{2+}$</td>
<td>(Y. Zhang, et al., 2013)</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>2-hydroxybenzaldehyde benzoylhydrazone</td>
<td>Al$^{3+}$, Ca$^{2+}$, Cd$^{2+}$, Fe$^{2+}$, K$^+$, Mg$^{2+}$, Na$^+$, Pb$^{2+}$, Zn$^{2+}$</td>
<td>(Espada-Bellido, Galindo-Riaño, García-Vargas, &amp; Narayanaswamy, 2010)</td>
</tr>
<tr>
<td></td>
<td>Rhodamine Schiff base</td>
<td>Li$^+$, Na$^+$, K$^+$, Ba$^{2+}$, Ca$^{2+}$, Cd$^{2+}$, Mg$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Fe$^{2+}$, Hg$^{2+}$, Fe$^{3+}$, Al$^{3+}$, Cr$^{3+}$</td>
<td>(Yang, et al., 2013)</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>Naphthaldehyde Schiff base</td>
<td>Fe$^{3+}$, Hg$^{2+}$, Ag$^+$, Ca$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Cr$^{3+}$, Mg$^{2+}$</td>
<td>(Wei, et al., 2013)</td>
</tr>
<tr>
<td></td>
<td>Vanillinyl thioether</td>
<td>Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, Hg$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Pb$^{2+}$, Pd$^{2+}$, Mn$^{2+}$, Al$^{3+}$, Cd$^{2+}$, Cu$^{2+}$, Fe$^{3+}$</td>
<td>(Patra, et al., 2016)</td>
</tr>
</tbody>
</table>

**CONCLUSION**

Schiff bases are considered as a very important class of organic compounds because of their ability to form complexes resulting in the application of sensor. The chemistry of Schiff bases is a field which is being noticed. In this review article, the applications of Schiff base type chemo sensors are summarized from the last ten years. The present paper leads us to conclude the significant role of Schiff base in the field of fluorescence sensors.


