

Fluorescence properties of some transition metal complexes of Schiff bases- A review

Abstract

In the last few years, there have been an increasing number of reports on the biological activity of metal complexes of Schiff bases; however, their applications in fluorescent probes have been scarce and largely limited to ruthenium complexes in DNA and oxygen sensing. This review includes studies on the photoluminescence behavior of metal complexes of Schiff bases and the effect of different metals on the intensity of fluorescence emission. The study would be beneficial for the design and development of metal based fluorescent sensors and light emitting devices.

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Introduction

Metal complexes with Schiff base ligands are promising materials for optical applications due to their ability to show enhanced photoluminescent properties, the ease of synthesis that readily permits structural modifications for optimization of material properties.¹⁻⁶ Motivated by the success of tris(8-hydroxyquinoline) aluminium in vacuum deposited LED'S, metal complexes have attracted a lot of attention and offer attractive light emission properties.⁷⁻⁸ In view of the above, we review the photo physical properties of metal complexes and their fluorescence behavior in comparison to the ligands.

Fluorescence studies

Metal complexes generate a greater diversity of tunable properties and exhibit their emission color by virtue of the coordinated metal center or by modifying the backbone substituents of ligands. Quenching of fluorescence of a ligands by transition metal ions during complexation is a rather common phenomenon which can be explained by processes such as magnetic perturbation, redox activity, electronic energy transfer, etc. Enhancement of fluorescence through complexation is however of great importance paving the way for increased photochemical applications of the complexes. In view of the above, we review the fluorescence behavior of some transition metal complexes.

A six-coordinated monomeric Co(II) complex with 4-(p-benzyloxy)-1,2,4-triazole has been synthesized and characterized by Zou et al on the basis of elemental analysis, IR, thermogravimetric analysis and X-ray diffraction technique.⁹ Structural analysis revealed octahedral environment around the Co(II) ion. The complex displayed enhanced fluorescence efficiency with strong blue emission in the solid state attributed to the more rigidity of the ligand coordinated to Co(II) ion that effectively reduces the loss of energy. A series of Co(II) complexes have been synthesized with Schiff bases derived from 3-substituted-4-amino-5-hydrazino-1,2,4-triazole by Avaji et al.¹⁰ Fluorescence of one Schiff base and its complex was investigated in various solvents. It was reported that complexation resulted in enhancement of fluorescence. Synthesis, crystal structure and photoluminescent properties of an aromatic bridged Schiff base ligand, N,n'-bis(4,4'-diethylamino) salicylidene)-1,2-phenylenediamine and its zinc(II) complex have been studied by Yu et al.¹¹ The zinc(II) complex was found to exhibit blue-green emission as a result of the fluorescence from the intraligand emission excited state and the maximum emission peaks

of the zinc(II) complex shifted to longer wavelength as the extended conjugation and rigid conformation of the ligand was increased. A series of Co(II), Ni(II) and Cu(II) complexes with Schiff bases derived from methylthiosemicarbazone and 5-formyl-6-hydroxy coumarin/8-formyl-7-hydroxy-4-methylcoumarin have been synthesized by Patil et al.¹² The photoluminescence properties of manganese (II), cobalt (II), cadmium (II), zinc(II) and copper(II) complexes of the Schiff base ligand, 5-methyl-1H-pyrazole-3-carboxylic acid(1-pyridin-2-yl-ethylidene)-hydrazide] have been studied by Konar et al.¹³ The ligand showed no considerable fluorescence at 314 nm while its zinc(II) and cadmium(II) complexes exhibited emissions at 522 and 510 nm, respectively. The Mn(II), Co(II) and Cu(II) complexes were fluorescence silent, like the ligand. It was reported that chelation induced rigidity played an important role in causing a change in the fluorescence behavior of the free ligand on complexation with the metal ions. A simple Schiff type fluorescent receptor prepared by the reaction of 2-hydroxynaphthalene-1-carboxaldehyde with tris(2-aminoethyl)amine was evaluated for its fluorescence response to heavy metal ions.¹⁴ It was found that the Schiff base receptor exhibits an off-on-type mode with high selectivity in the presence of Zn(II) ion. The enhanced fluorescence is a consequence of combined effects of chelation, C=N isomerization and inhibition of photo induced electron transfer (PET). Cobalt, nickel, copper and zinc complexes of bidentate Schiff base derived from the condensation of 4-cyanobenzaldehyde with 4-amino-3-mercapto-5-oxo-1,2,4-triazine were studied for their fluorescence behavior by Singh et al.¹⁵ The fluorescence spectra results revealed that fluorescence emission intensity of Schiff bases decreased dramatically on complex formation and the zn(II) complexes showed highest emission maxima followed by cu(II), co(II) and ni(II).

Conclusion

The review mainly focuses on metal enhanced fluorescence of transition metal complexes. The increased photoluminescence of the metal complexes in comparison to the ligand may be due increased rigidity in structure of the complexes thereby offering potential applications of these complexes in sensors, light emitting diodes, phytodynamic cancer therapy and many other photochemical processes.

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Conflict of interest

The authors declare that there is no conflict of interest.

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