



Synthesis, Characterization and Photophysical Study Of 2,2'-{(4-Subbenzene-1,2-Diyl)[Nitrilo(E)Methylydene]}Diphenol and Their Zn (II) Complexes.

D. L. Arakh¹, T. M. Bhagat²

¹Department of Physics, G. S. Gawande College, Umarched, Yawatmal, Maharashtra, India

²P.G. Department of chemistry G. S. Gawande College, Umarched, Yawatmal, Maharashtra, India

ABSTRACT

The introduction of various substituents into the structure of organic ligands affects photoluminescence spectra of ligand and their Zinc (II) complexes. These ligands are tetradentate schiff bases derived from salicylaldehyde and the derivatives of ortho phenylenediamine. The photophysical properties were characterised by excitation and emission spectra which shows the color tunable property with the Zn(II) complex. The synthesised ligand and its Zn (II) complexes were also characterised by NMR Spectroscopy, Mass spectroscopy, TGA and DTA. They had good thermostability, solubility, and can be used as organic electroluminescent materials.

Keywords : O-phenylenediamine, Zn (II) complexes, NMR, DSC & Photophysical properties.

I. INTRODUCTION

The field of organic electronic is an active emerging technology with immense promise for innovative, convenient & high performance electronics. Because of remarkable properties of the organic materials as Schiff bases & their metal complexes, they can be used to make a wide range of electronic devices as OLEDs. The properly chosen substituents will allow us to shift the emission wavelength. This approach of color tuning is important for preparation of full color displays that require Red, Blue and Green emitting pigments. The electron donating groups & electron withdrawing groups when introduced to organometallic electrolumophore cause change in electronic properties of ligand involved in emission of light. The introduction of functional group may therefore be used to fine tune the luminescence of electrolumophore. This approach may be successfully used to change a color of OLED elements.

In 2000, T. Tsutsui et al. reported a series of zinc chelates with arene substituted oxadiazole ligands, which showed good color-tunability from blue to orange

by adjustment of different substituents. Salophens are one of the oldest and most popular class of ligands in coordination chemistry because of their versatility and easy synthetic availability. They are diimino tetradentate Schiff bases derived from the condensation of 1,2-phenylenediamine, or of its derivatives, with two equivalents of salicylaldehyde. A large number of synthetic routes to ortho-substituted phenols and to the corresponding ortho salicylaldehydes gives access to a large variety of structures with subtle variations in the steric and electronic configuration. For these reasons they have been extensively used to coordinate transition and main group metals. Because salicylaldehyde Schiff base zinc (II) chelate could be synthesized and chemically modified easily, thus may lead to cutdown cost. As it has excellent fluorescent properties, and was proved to be excellent organic electroluminescent materials, we choose it as parent, and try to achieve color-tunability through variation of substituents in the ligands. The results indicated that they and their metal complexes could emit strong fluorescence with colors varied with different substituents.

II. EXPERIMENTAL SECTION

Synthesis of Ligands

Add 2.4gm of Salicylaldehyde (2 mmol) (2) in 10 ml of absolute alcohol and for few minutes till all aldehyde get dissolve. Add 1 mmol of (chloro,methyl) Ortho phenylene diamine in above reaction mixture with constant stirring and finally add catalytic amount of acetic acid. Reflux the reaction mixture with stirring for about 30 – 50 minutes and check the completion of reaction with help of TLC (in pet ether and ethyl acetate). Cool the reaction mixture and filter the resulting solid on Buckner funnel, wash with cold ethanol. Record the yield, M.P and recrystallized from absolute ethanol.

Synthesis of Zn complex

The complexes were prepared by heating under reflux a 1:2 molar mixture of schiff bases and equivalent mol of ZnCl₂ in ethanol(10 ml) for 1 hour. Add equivalent mol

of KOH to reaction mixture drop by drop till the yellowish precipitate were formed.the precipitates formed wre then seperate out,filtered off and finally dried under vaccumat 50-60 °C.The yield was in the range 70-80%.

Scheme:

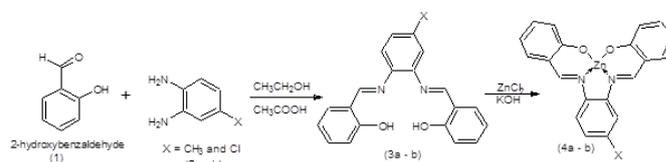


Table 1. Properties of chelating agent

Starting Amine	Structure & IUPAC Name of product	Yield	M. P. °C	NMR data (δ in ppm) in DMSO-D ₆ (300 MHz)
4-chloro 1,2-phenylene diamine	2,2'-{(4-chlorobenzene-1,2-diyl)bis [nitriolo(<i>E</i>)methylidene]}diphenol (chloro-sal)	62%	132	6.94(m,4H), 7.32(d,1H), 7.5 (s, 1H) 7.45(d,1H), 8.94(s,2H),12.90(bs,2H)
4-methyl 1,2-phenylene diamine	2,2'-{(4-methylbenzene-1,2-diyl)bis [nitriolo(<i>E</i>)methylidene]}diphenol (methyl-sal)	78%	101	2.39(s,3H),6.92(m,4H) 7.26(d,1H), 7.12(d,1H), 7.36(s,1H), 8.37(m,2H), 12.95(s,2H).

Luminescence Properties

Luminescence properties of the schiff bases of Salicylaldehyde with various diamines (chloro, methyl) has been checked by using Spectrofluorometer model number RF5301. A Xe laser lamp was used for excitation and emission spectra were scanned from the

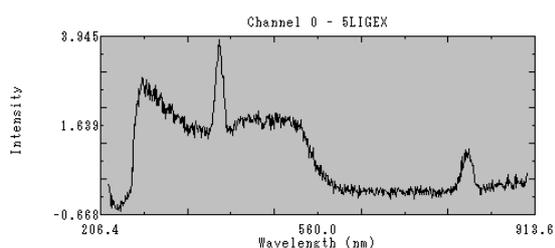
range 220 nm to 750 nm. For fluorescence study of the Schiff bases, dimethyl formamide is used as solvent and reference material. The excitation of the molecule is occurred due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

The fluorescence data can be shown in following data:

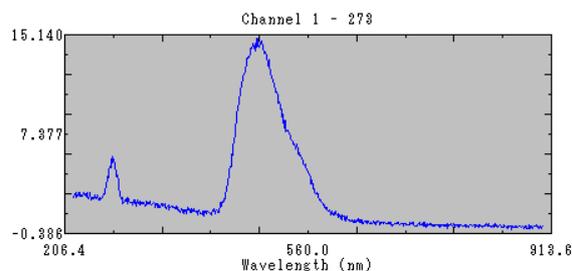
width: Excitation and emission is 5 nm; Concentration of solution is 500 ppm; Solvent used is DMF.

Sample name	Excitation wavelength (nm)	Emission wavelength (nm)
Chloro-salophene	273(ϵ 2.87)	486(ϵ 14.83)
Methyl-salophene	305(ϵ 2.62)	468(ϵ 37.79)
Zn(Chloro-sal)	275(ϵ 4.72)	510(ϵ 130.62)
Zn(Methyl-sal)	305(ϵ 4.72)	500(ϵ 155.96)

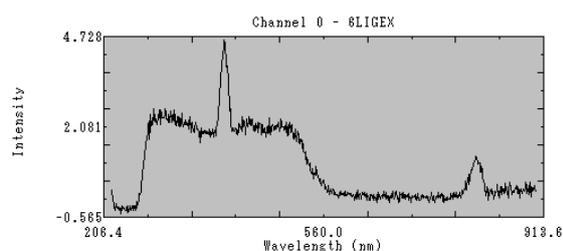
Cl-salophen ligand excitation at 273 nm



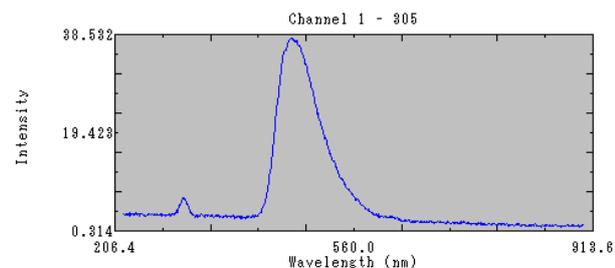
Cl-salophen ligand emission



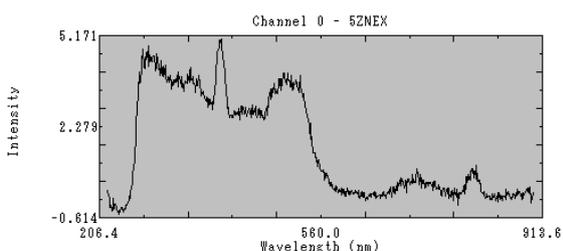
Me-salophen ligand excitation at 305 nm



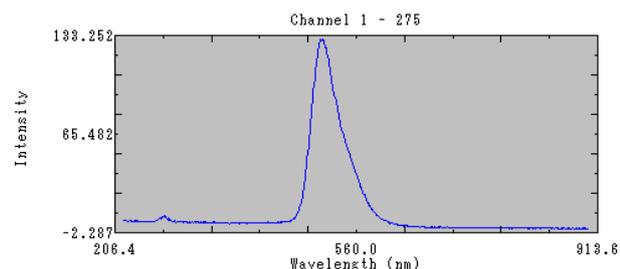
Me-salophen ligand emission



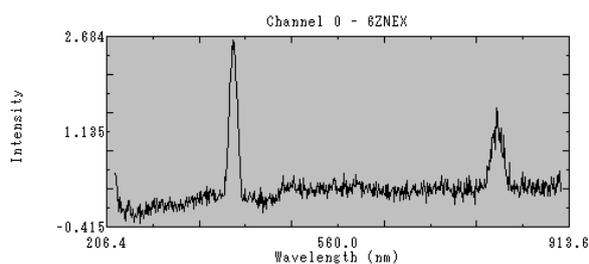
Zn(Cl-salophen) complex excitation at 275 nm



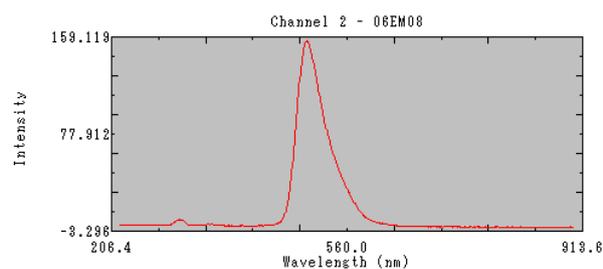
Zn(Cl-salophen) complex emission



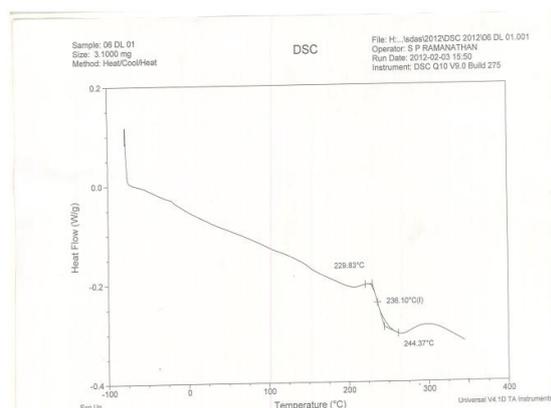
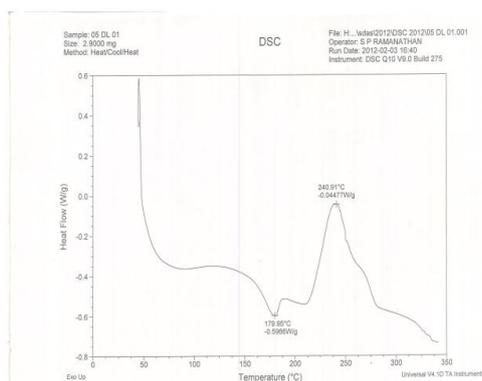
Zn(Me-salophen) complex excitation at 305



Zn(Me-salophen) complex emission



TGA/DSC



Most interestingly, DSC analyses reveal that the complexes are able to form amorphous glasses with reasonably high glass transition temperatures ($T_g=229.83^{\circ}\text{C}$ – 244.37°C) upon cooling of melt samples of methyl-salophen ligand and when a crystalline sample of the complex of Cl-salophen ligand obtained by crystallization from a $\text{CH}_2\text{Cl}_2/n$ -hexane solvent mixture is heated, two distinct melting transitions take place at 179.95°C and 240.91°C . The first is followed by instant crystallization at around 179.95°C to form the second crystal, which melts at 240.91°C .

III. RESULT AND DISCUSSION

In the both ligands aldehyde peak is absent in NMR data and peak of $-\text{CH}=\text{N}$ is observed at 8.94. It shows that the product is formed.

IV. CONCLUSION

The interesting outcome of this work is, the both ligands shows the blue light emission region. but with zinc metal its shows the bluish green light emission region.

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