Characterization and luminescent properties of zinc–Schiff base complexes for organic white light emitting devices

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Characterization and luminescent properties of zinc–Schiff base complexes for organic white light emitting devices

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Abstract: Zinc complexes with Schiff base ligands bis(salicylidene)ethylene-1,2-diamine (salen), bis(salicylidene)propylene-1,3-diamine (salpen), bis(salicylidene)butylene-1,4-diamine (salbutene), bis(salicylidene)hexylene-1,6-diamine (salhexene), bis(salicylidene)heptylene-1,7-diamine (salheptene) were synthesized and characterized. All these metal complexes exhibited high thermal stability. The photo-physical properties of zinc complexes were investigated by taking their UV–vis absorption and photoluminescent spectra. The complexes of Schiff bases with zinc gave blue luminescence (430–450 nm) under excitation of ultraviolet energy source which can be efficiently used for the generation of white light for display applications.

Subjects: Chemistry; Inorganic Chemistry; Materials Chemistry

Keywords: luminescence; characterization; zinc–Schiff base complexes; blue emission

1. Introduction

Organic light-emitting device (OLED) developed with Tris(8-hydroxyquinolinato)aluminum (Alq3) (Tang & VanSlyke, 1987) paved the path to search metal complexes to produce all colors in the visible spectrum for the optoelectronic devices. Organic compounds complexed with metals can easily be tuned to produce the desired emission through different substituents. Zinc complexes are important as light-emitting materials (Hamada et al., 1993; Kim, Kim, Shin, Kim, & Ha, 2001; Tao et al., 1997; Yu, Liu, Song, Wu, & Zhu, 2001) as well as exhibit electron transport ability, light-emitting efficiency, high thermal and redox stability and tunable electronic properties (Bhattacharjee, Das, Mondal, & Rao, 2010; Pucci et al., 2009), ternary complexes as electron transport and electroluminescent materials (Kumar et al., 2013).
Transition metal complexes with Schiff bases have been studied extensively because of their easy synthesis, high thermal stability, and use in many applications as analytical reagents (Cimernman, Galic, & Bosner, 1997). These also serve in oxygen storage devices (Chantarasiri, Tuntulani, Tongraung, Magee, & Wannatong, 2000), molecular architectures (Costamagna, Vargas, Lattorre, Alvrado, & Mena, 1992), OLED applications, lasers, transistors, and fluorescent sensors (Eltayeb, Teon, Adnan, Tech, & Fun, 2011; Garnovskii, Nivorozhkin, & Minkin, 1993; Kim, Kim, & Sohn, 2001; Yu et al., 2006, 2008). Substituted Schiff base complexes with zinc metal exhibit good photoluminescent (PL) and electroluminescent properties. Luminescence properties of zinc(II) complexes originate from organic ligand rather than LMCT because d shell of central ion is completely filled (Basak et al., 2007). Molecular structures, degree of conjugation, and substitutes of ligands have a large effect on PL characteristics of zinc–Schiff base complexes. Zinc complexes based on salicylidimino Schiff base ligands emit light in blue (Costamagna et al., 1992), green (Eltayeb et al., 2011), and red region (Luizzu, Oberhauser, & Pucci, 2010). These compounds show good color purity and there is a possibility to incorporate them in the list of electroluminescent complexes used for the fabrication of full colored OLEDs. Nonetheless, blue light-emitting zinc complexes are rare compared to green and yellow green light-emitting materials (Son et al., 2008; Wu, Lavigne, Tao, D’Iorio, & Wang, 2000).

White light emission can be obtained by using orange dye and blue light-emitting materials (Kumar et al., 2010). Also, blue light-emitting zinc complexes can be used as dopant materials for the production of white light; recently, Schiff base zinc complexes have been used for fabrication of white light emitting devices (Dumur et al., 2014). Zinc complexes with bissalicylidenehexylenediamine (Hamada et al., 1993), N,N-bis salicylideneethylenediamine (Vashchenko et al., 2010), and bis(salicylidene)propylene-1,3-diamine (Nishal et al., 2014) are also reported as electroluminescent emissive materials.

Here in this communication, we present a series of luminescent zinc–Schiff base complexes using organic ligands prepared with different spacer diamines and salicylaldehyde. The compounds were characterized with various analysis techniques. The luminescent properties of metal complexes were analyzed by UV–visible absorption and PL emission spectroscopy.

2. Experimental

2.1. Materials
Salicylaldehyde, ethylene-1,2-diamine, propylene-1,3-diamine, butylene-1,4-diamine, hexylene-1,6-diamine, heptylene-1,7-diamine were purchased from Fluka. High-purity reagent-grade chemicals and solvents were used without further purification.

2.2. Instrumentations
The elemental analysis of C, H, N were performed on Elemental Analyzer Perkin-Elmer 2400 CHN. IR spectra were recorded with FTIR Model Alpha Bruker of Germany. 1H NMR spectra were run on FT NMR Spectrometer model Avance-II (Bruker). Thermal gravimetric analyses (TGA) were carried on the Perkin Elmer STA-6000 instrument. The excitation and emission spectra of complexes were taken in methanol solvent using Horiba Jobin YVON spectrophotometer and Fluolog Model FL 3-11 spectrometers, respectively.

2.3. Synthesis of the Schiff bases
Schiff bases were synthesized according to general procedure taking a methanolic solution of salicylaldehyde and diamines (ethylene-1,2-diamine/propylene-1,3-diamine/butylene-1,4-diamine/hexylene-1,6-diamine/heptylene-1,7-diamine) in 2:1 M proportion. The mixture was refluxed at 60°C for 2 h. After completion of reaction, the off-white precipitates formed were filtered and washed with deionized water. The compound was recrystallized with methanol and dried in oven. The yield of products was ~80–90%.
2.4. Synthesis of Schiff base–zinc complexes

The metal complex was prepared by reaction of Schiff base ligand with zinc acetate (ligand and metal) in 1:1 M ratio in methanol. The Schiff base ligand salen (1 mM)/salpen (1 mM)/salbutene (1 mM)/salhexene (1 mM)/salheptene (1 mM) was separately taken in 50 ml methanol and heated on a magnetic stirrer at 60°C for 1 h. The aqueous solution of zinc acetate (1 mM) was added dropwise to the flask with magnetic stirring. The mixture was kept at 60°C temp for 2 h on magnetic stirrer. After completion of the reaction, cream-colored precipitate of the respective complex separated from the reaction mixture which were filtered, washed with deionized water, ethanol and dried at 100°C (Scheme 1).

All the zinc complexes were sparingly soluble in methanol and showed good solubility in DMSO.

3. Results and discussion

The Schiff base complexes [Zn(salen)], [Zn(salpen)] and [Zn(salhexene)] have been previously reported. Here we synthesized above zinc complexes and related new Schiff base complexes of zinc [Zn(salbutene) and Zn(salheptene)] using different spacers. Complexes were further characterized and confirmed by various spectroscopic techniques (Table 1).

3.1. Thermal characteristics

The thermal properties of metal complexes were studied by TGA to investigate thermal stability of prepared zinc complexes of Schiff bases. The TGA of zinc metal complexes was taken over a temperature range from 25 to 600°C at a scan rate of 10°C/min in nitrogen atmosphere. All the prepared complexes of zinc exhibited high thermal stability as shown in Figure 1. The onset temperature of weight loss was greater than 320°C for all zinc complexes except [Zn(salbutene)]. Above 380°C, all

| S. No. | Compound       | $\nu$(O–H) | $\nu$(C–H) | $\nu$(C=N) | $\nu$(C–O) |
|-------|----------------|-----------|-----------|-----------|-----------|
| 1     | (salen)        | 3050      | 2955      | 1678      | 1219      |
| 2     | (salpen)       | 3051      | 2944      | 1645      | 1209      |
| 3     | (salbutene)    | 3051      | 2944      | 1672      | 1210      |
| 4     | (salhexene)    | 3066      | 2964      | 1633      | 1214      |
| 5     | (salheptene)   | 3070      | 2984      | 1646      | 1212      |
| 6     | [Zn(salen)]    | –         | 2944      | 1620      | 1197      |
| 7     | [Zn(salpen)]   | –         | 2938      | 1622      | 1195      |
| 8     | [Zn(salbutene)]| –         | 2912      | 1622      | 1186      |
| 9     | [Zn(salhexene)]| –         | 2930      | 1624      | 1186      |
| 10    | [Zn(salheptene)]| –        | 2931      | 1625      | 1185      |
Figure 1. Thermogravimetric curves of zinc complexes.

Figure 2. UV–visible absorption spectra of zinc complexes with Schiff bases at $10^{-4}$ M concentration in DMSO solvent.

Table 2. Photo-physical data of zinc–Schiff base complexes at $10^{-4}$ M concentration

| S. No. | Compound          | UV–vis (nm) | PL at excitation wavelength of $(n \rightarrow \pi^*)$ | CIE   | Relative | TGA (°C) |
|--------|-------------------|-------------|----------------------------------------------------|-------|----------|----------|
|        |                   | $\pi \rightarrow \pi^*$ | $n \rightarrow \pi^*$ | $\lambda_{max}$ | $X$ | $Y$ | PL:QE |        |
| 1      | [Zn(salen)]       | 262         | 352                                               | 447   | 0.15     | 0.11     | 1.05    | 350    |
| 2      | [Zn(salpen)]      | 263         | 349                                               | 440   | 0.15     | 0.11     | 1.17    | 380    |
| 3      | [Zn(salbutene)]   | 269         | 364                                               | 436   | 0.15     | 0.07     | 1.055   | 280    |
| 4      | [Zn(salhexene)]   | 273         | 384                                               | 433   | 0.15     | 0.09     | 1.077   | 370    |
| 5      | [Zn(salheptene)]  | 272         | 363                                               | 430   | 0.15     | 0.13     | 1.268   | 380    |
the complexes lost their weight and decomposed. These studies showed that all metal complexes exhibited good thermal stability and it is expected that no decomposition will take place during their other analysis and applications.

Figure 3. PL spectra (Taken at $10^{-4}$ M concentration in DMSO solvent) and photographs of zinc–Schiff base complexes under UV radiation (365 nm).

Figure 4. CIE chromaticity diagram of prepared zinc complexes of Schiff bases.
3.2. UV–visible absorption and luminescent characterization

The UV–visible absorption bands of zinc complexes matched closely with the protonated ligand precursor. The electronic absorption spectra of zinc complexes showed metal perturbed ligand centred $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions (Aazam, Husseiny, & Al-Amri, 2012). Upon excitation at absorption wavelengths, the complexes fluoresced in visible region of the spectrum. The ultraviolet
absorption and PL emission spectra of synthesized metal complexes were recorded in DMSO solvent using \(10^{-4}\) molar concentration of solute. Absorption spectra of zinc complexes are shown as curves A, B, C, D, and E in Figure 2. The detail of absorption bands due to various ligand-centered electronic transitions are mentioned in Table 2. The molar absorptivity of zinc complexes [Zn(salen)], [Zn(salpen)], [Zn(salbutene)], [Zn(salhexene)], and [Zn(salheptene)] were 11690, 8452, 12080, 2397, 592 \(\text{M}^{-1}\ \text{cm}^{-1}\), respectively, at absorption wavelength.

On excitation at these wavelengths, these materials fluoresced at 447, 440, 436, 433, and 430 nm, respectively, in visible region as shown in Figure 3. The complexes showed good luminescence in solid state as well as solution state. Since there are no d–d transitions in zinc complexes, hence the emission of light is assigned as relaxation from higher energy level to lower energy level due to intra-ligand transitions.

Images showing emission of light in solid state under UV light are also shown in Figure 3 and all photo-physical properties are presented in Table 2. Here we are using different bridging groups, i.e. diamines for Schiff base synthesis. The PL properties of the complexes change with change in these bridging groups. The increase in number of alkyl groups in bridging diamines result in slight blue shift in emission wavelengths of metal complexes. This shift may be due to slight decrease in conjugation and increase in band gap between excited and ground states of complexes.

The color coordinates for the zinc complexes were calculated from emission spectra. The value of \(x\) and \(y\) coordinates are shown in Table 2 and also in Figure 4.

The relative PL quantum yield of metal complexes was calculated based on Alq\(_3\) as standard and using the following equation:

\[
\Phi_f(x) = \frac{A_x}{A_s} \left( \frac{F_x}{F_s} \right) \left( \frac{n_x}{n_s} \right)^2 \Phi_f(S)
\]

where \(\Phi_f\) is the fluorescence quantum yield, \(A\) is the absorbance at the excitation wavelength, \(F\) is the area under emission curve, and \(n\) is the refractive index of the solvents used. Subscripts s and x refer to the standard and sample, respectively (Forgues & Lavabre, 1999).

The results are summarized in Table 2, the PL quantum yield of [Zn(salen)] and [Zn(salheptene)] complexes was found to be higher than other prepared zinc complexes of this series and with Alq\(_3\) as suggested by other reports (Ghedini, Deda, Aiello, & Grisolia, 2003). The optical band gap energy was calculated from absorption spectrum (Singh et al., 2011). Figure 5(a)–(c) shows square of absorption vs. energy for the synthesized zinc complexes. The optical band gap energy was found to be 3.14, 3.15, 3.04, 2.8, and 3.08 eV for [Zn(salen)], [Zn(salpen)], [Zn(salbutene)], [Zn(salhexene)], and [Zn(salheptene)], respectively.

The results showed that the zinc–Schiff base complexes could be suitably used as blue light-emitting materials for generating white light for various optoelectronic applications (Kumar et al., 2010).

4. Conclusions

A series of Schiff base ligands of salicylaldehyde with different diamines were synthesized and their complexes with zinc were prepared. These synthesized complexes emitted blue light (430–450 nm) under UV radiations. On increasing the number of alkyl groups in bridging chain, there was slight decrease in conjugation chain and blue shift in emission wavelengths was observed. This was done to tune the color for full color displays and to use these metal complexes as emissive materials in OLEDs. The results show that the metal complexes can be used as good blue light-emitting source which can be suitably used for generation of white light for optoelectronic display device applications.
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