

Transition Metal Complexes of Pyridyl Ligand as Light Emitting Materials in OLEDs

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Transition metal complexes, viz., tetrapyridylbis(isothiocyanato)nickel(II) (**1**), dipyridylbis(isothiocyanato)copper(II) (**2**) and dipyridylbis(isothiocyanato)zinc(II) (**3**) were synthesized by conventional methods. All the synthesized metal complexes were characterized by spectral and elemental analysis. Diffused reflectance (DR) spectra of the complexes **1-3** recorded in the range 200-1100 nm exhibit major peaks at 450 nm and 750 nm (% diffused reflectance 50 and 55, respectively) for complex **1**, 500 nm (20 % diffused reflectance) for complex **2** and 400 nm (50 % diffused reflectance) for complex **3**. The excitation and emission peaks obtained from photoluminescence spectra indicated the emission of white, green and white lights by the complexes **1**, **2** and **3**, respectively. From diffused reflectance spectra, the measured band gap energies were found to be 3.95 eV for complex **1**, 2.77 eV for complex **2** and 4.3 eV for complex **3**. Commission Internationale de l'Eclairage (CIE) coordinates of (0.31533, 0.33082), (0.22605, 0.35099) and (0.28633, 0.31012) were calculated for the complexes **1**, **2** and **3**, respectively. The phosphors **1-3** were readily soluble in various common organic solvents and they could become promising light emitting materials in organic light emitting diodes (OLEDs).

Keywords: Transition metal complex, Pyridyl ligand, Charge transfer, Light emitting materials, OLED.

INTRODUCTION

An organic light emitting diode (OLED), a solid state device, is a light emitting diode in which the emissive electroluminescent layer happens to be a film of an organic compound that emits light in response to electric current. After the successful reporting of the first high efficiency OLED by Tang and Vanslyke [1], the development of light emitting devices solely based on organic ligands has been the subject of considerable attention because of their potential to replace traditional light sources and displays [2-6]. The electroluminescent devices based on organic materials have gathered much attention due to their attractive characteristics and potential applications in flat panel displays [7]. Many of the transition metal complexes were found to exhibit potential applications in the development of energy-efficient, low-cost and full colour flat panel OLED displays, thereby revealing excellent photoluminescent and electroluminescent properties [8-12]. These complexes were found to display

excellent electron-transport and light emission properties, high thermal stability and ease of sublimation [13,14]. The use of transition metal cadmium complexes such as Cd(phen)q and Cd(bpy) in OLED applications was investigated by studying their photoluminescent properties [15,16]. Blue light emitting Zn(II) complexes involving a phenylbenzimidazole ligand and green-emitting Zn(II) complexes with benzothiazole and its derivatives as ligands have been investigated [17,18]. Because of their considerable flexibility and high stability in design structure and modification, the luminescent transition metal complexes have been the focus of current research for application in OLEDs [19]. The demonstration by recent research in optoelectronics the high potential of Cu(I) thiocyanate (CuSCN) as a universal hole-transport interlayer material in organic light-emitting diodes (OLEDs) was reported [20]. Organic light-emitting diodes (OLEDs) with white light emission (WOLEDs) are promising materials in the future for energy-saving light sources due to their low driving voltage,

high brightness and high efficiency [21-23]. Emissive materials are the vital functional components of OLEDs and are therefore the subject of extensive research in recent years. The conventional materials with fluorescence emission make use of only singlet excitons, leaving the triplet excitons unharnessed. The phosphorescent (triplet) emitters are generally constructed by transition metal complexes with organic ligands as a result of chelation.

With special reference to present work, nitrogen atoms of pyridyl ligands serve as potential donor atoms to form stable coordination complexes with several transition metals. These ligands used in complexes play a major role as the conduction in organic layer is reported to be caused by delocalization of π -electrons throughout or part of organic molecules. The ready solubility of aforesaid complexes in solvents such as THF, DMF, DMSO, CHCl_3 and CH_3CN could also play an important role in making a film in the emissive layer of the OLED device by different techniques. Herein, the synthesis and study of photophysical properties of tetrapyridylbis(isothiocyanato)nickel(II) (**1**), dipyridylbis(isothiocyanato)copper(II) (**2**) and dipyridylbis(isothiocyanato)zinc(II) (**3**) through photoluminescence and diffused reflectance spectra are reported. The enhanced polarity and stability due to the incorporation of thiocyanate ligands of the aforementioned complexes could make them efficient light emitting materials in OLEDs.

EXPERIMENTAL

Commercially available chemicals & reagents purchased from Sigma-Aldrich were used for the synthesis of complexes. All the solvents were of reagent grade and employed in the reactions without further purification. The melting points of the complexes were determined by electrothermal apparatus in an open capillary and are uncorrected. The FT-IR spectra were recorded on a Jasco FT-IR spectrometer by KBr pressed pellet technique. The percentage of the elements C, H, N and S was analyzed using the Elementar Vario EL III analyser. Mass spectra of the samples were recorded using Shimadzu LC-2010EV with ESI (electron spray ionization) probe. The recording of diffused reflectance spectra were done using Perkin-Elmer UV-Visible Spectrophotometer Lambda-35. The photoluminescence (PL) spectra were performed on a Spectrofluorimeter, Moriba equipped with 450 W Xenon lamp as an excitation source. Scanning electron microscopy (SEM) pictures were obtained using Hitachi table top, Model TM 3000.

Synthesis of tetrapyridylbis(isothiocyanato)nickel(II) complex (1): Nickel(II) chloride hexahydrate (2.37 g, 0.01 mol) was dissolved in 40 mL distilled water in a 100 mL round bottom flask. To that, 4 mL pyridine was added and the reaction mixture was stirred on a magnetic stirrer. Ammonium thiocyanate (1.52 g, 0.02 mol) dissolved in 15 mL of distilled water was slowly added to the above solution and the resulting mixture was stirred at room temperature until a blue coloured precipitate was obtained. The precipitate was allowed to cool in an ice bath for 15 min and then filtered through Büchner funnel. The solid product was washed with 3-5 mL portions of ethanol-pyridine (9:1) solution and dried. The blue coloured complex was then stored in a desiccator until constant weight obtained. Yield: 91.2 %; m.p.: 260-262 °C; FT-IR (KBr, cm^{-1}): 2082 cm^{-1} ($\text{C}\equiv\text{N}$ stretching of Ni-NCS), 1600 cm^{-1} ($\text{C}=\text{C}$ arom.), 1442

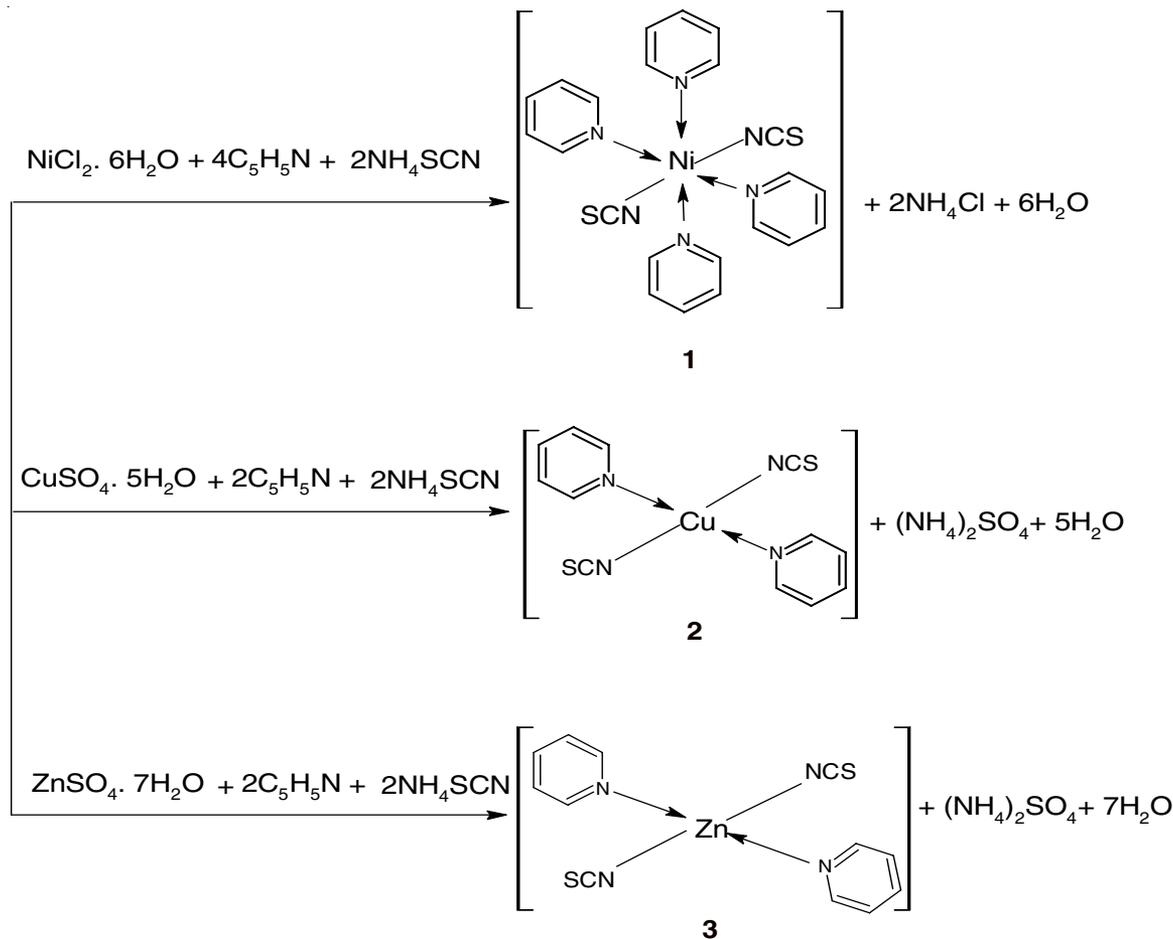
cm^{-1} ($\text{C}=\text{N}$ arom.), 699.1 cm^{-1} (Ni-N bending). Elemental analysis of $\text{C}_{22}\text{H}_{20}\text{N}_6\text{S}_2\text{Ni}$ calcd. (found) %: C: 53.80 (53.76); H: 4.07 (3.62); N: 17.11 (17.04); S: 13.04 (11.95). MS (m/z): calcd. 491.25, found 492.07 [$\text{M}+1$].

Synthesis of dipyridylbis(isothiocyanato)copper(II) complex (2): To a copper(II) solution obtained by dissolving copper(II) sulphate pentahydrate (2.49 g, 0.01 mol) in 40 mL distilled water in a 100 mL round bottomed flask, 2 mL pyridine was added with stirring on a magnetic stirrer. Ammonium thiocyanate (1.52 g, 0.02 mol) dissolved in 15 mL distilled water was slowly added to the above solution. The resulting mixture was stirred at room temperature until a green coloured precipitate was obtained. The precipitate was allowed to cool in an ice bath for 15 min and then filtered through Büchner funnel. The solid product was washed with 3-5 mL portions of ethanol-pyridine (9:1) solution and dried. The green coloured complex was then stored in a desiccator until constant weight was obtained. Yield: 80.6 %; m.p.: 190-192 °C; FT-IR (KBr, cm^{-1}): 2093 cm^{-1} ($\text{C}\equiv\text{N}$ stretching of Cu-NCS), 1602.6 cm^{-1} ($\text{C}=\text{C}$ arom.), 1444 cm^{-1} ($\text{C}=\text{N}$ arom.), 692.3 cm^{-1} (Cu-N bending). Elemental analysis of $\text{C}_{12}\text{H}_{10}\text{N}_4\text{S}_2\text{Cu}$ calcd. (found) %: C: 42.66 (40.34); H: 2.98 (2.75); N: 16.58 (16.55); S: 18.97 (18.61). MS (m/z): calcd. 337.90, found 337.81 [M^+].

Synthesis of dipyridylbis(isothiocyanato)zinc(II) complex (3): To a zinc(II) solution obtained by dissolving zinc(II) sulphate heptahydrate (2.87 g, 0.01 mol) in 40 mL distilled water in a 100 mL round bottomed flask, 2 mL pyridine was added with stirring on a magnetic stirrer. Ammonium thiocyanate (1.52 g, 0.02 mol) dissolved in 15 mL distilled water was slowly added to the reaction mixture, which was stirred at room temperature until a white coloured precipitate was obtained. The precipitate was allowed to cool in an ice bath for 15 min and then filtered through Büchner funnel. The solid product was washed with 3-5 mL portions of ethanol-pyridine (9:1) solution and dried. The white coloured complex was then stored in a desiccator until constant weight was obtained. Yield: 90.2 %; m.p.: 210-211 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm): 8.569-8.584 (d, 2H, pyridyl CH), 7.794-7.831 (m, 2H, pyridyl CH), 7.411 (t, 1H, pyridyl CH); FT-IR (KBr, cm^{-1}): 2097 cm^{-1} (CN stretching of Zn-NCS), 1608.3 cm^{-1} ($\text{C}=\text{C}$ arom.), 1445.4 cm^{-1} ($\text{C}=\text{N}$ arom.), 697.1 cm^{-1} (Zn-N bending); Elemental analysis of $\text{C}_{12}\text{H}_{10}\text{N}_4\text{S}_2\text{Zn}$ calcd. (found) %: C: 42.42 (42.15); H: 2.96 (2.91); N: 16.49 (16.12); S 18.87 (18.36); MS (m/z): calcd. 339.74, found 339.25 [M^+].

RESULTS AND DISCUSSION

In the present work, pyridyl complexes such as tetrapyridylbis(isothiocyanato)nickel(II) (**1**), dipyridylbis(isothiocyanato)copper(II) (**2**) and dipyridylbis(isothiocyanato)zinc(II) (**3**) were synthesized by the direct reaction of respective metal salts in which the metal was in +2 oxidation state and pyridine in the presence of an ambidentate ligand NCS (isothiocyanate) [24,25]. The method of synthesis is shown in **Scheme-I** and good yields were achieved with respect to synthesis. The synthesized complexes were analyzed by determining their melting points, recording of their IR spectra and by the determination of percentages of C, H, N and S elements. The formation of each complex was primarily confirmed by the change in colour and by the determination of melting point.



Scheme-I: Synthesis of metal complexes containing pyridyl ligands

Infrared spectra of the metal complexes showed the shifting of absorption bands relative to those in the IR spectra of free ligands. The data on the composition of complexes obtained by CHNS analysis clearly indicated the formation of said structures. Mass spectral analysis confirmed the mass of all the synthesized complexes and the structure of complex **3** was further confirmed by proton NMR spectrum owing to its diamagnetic nature. Complexes **1** and **2** were not amenable for characterization by NMR due to their paramagnetic nature.

In complex **1**, Ni(II) is coordinated to two terminal N-bonded thiocyanato anions and four neutral pyridyl ligands, whereas in complexes **2** and **3**, Cu(II) and Zn(II) are coordinated to two terminal N-bonded thiocyanato anions and two neutral pyridyl ligands [26,27]. Based on the nature of metal and by the spectral analysis, the geometries predicted for the complexes were octahedral for Ni(II) complex (**1**) and square planar for Cu(II) and Zn(II) complexes (**2** and **3**). Two NCS ligands in the above metal complexes (**1-3**) were linked to metal through anionic type of bonding. Thiocyanate or isothiocyanate ligands are reported to stabilize the metal complex and are believed to control the λ_{\max} and absorptivity. In accordance with the principle of HSAB, nitrogen of thiocyanate, being smaller and more electronegative than sulphur, tends to coordinate strongly to Cu^{2+} . While the delocalized molecular orbitals of pyridine can act as π -acceptors, excited state of the metal ion can transfer electron density into the pyridine ligand through metal to ligand charge transfer (MLCT) transition [28].

Diffused reflectance spectra: Diffused reflectance (DR) spectra of complexes **1-3** measured in the range 200-1100 nm are shown in Fig. 1. While the DR spectrum of complex **1** exhibited major peaks at 450 nm (50 % diffuse reflectance) and 750 nm (55 % diffuse reflectance), complex **2** showed a major peak at 500 nm (20 % diffuse reflectance). For complex **3**, a peak was appeared at 400 nm (50 % diffuse reflectance). Kubelka-Munk theory was used to determine the energy band gap of complexes **1-3** from the respective DR spectra. The intercepts of the tangents to plots of $[F(R_{\infty})hv]^{1/2}$ versus photon energy hv are shown in Fig. 1b. The Kubelka-Munk function $F(R_{\infty})$ and photon energy (hv) were calculated by using the equations given below:

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (1)$$

$$hv = 1240/\lambda \quad (2)$$

where R_{∞} = reflection coefficient of the sample, λ = absorption wavelength. The band gap energies were found to be 3.95, 2.77 and 4.30 eV for complex **1**, **2** and **3**, respectively. It indicated that interband transitions are due to spectroscopically allowed direct transitions. The reaction conditions and preparation methods will decide the E_g values that could favour or inhibit the structural defect formation. Structural defects are able to control the degree of structural order-disorder of the substance and consequently the number of intermediary energy levels within the band gap [29].

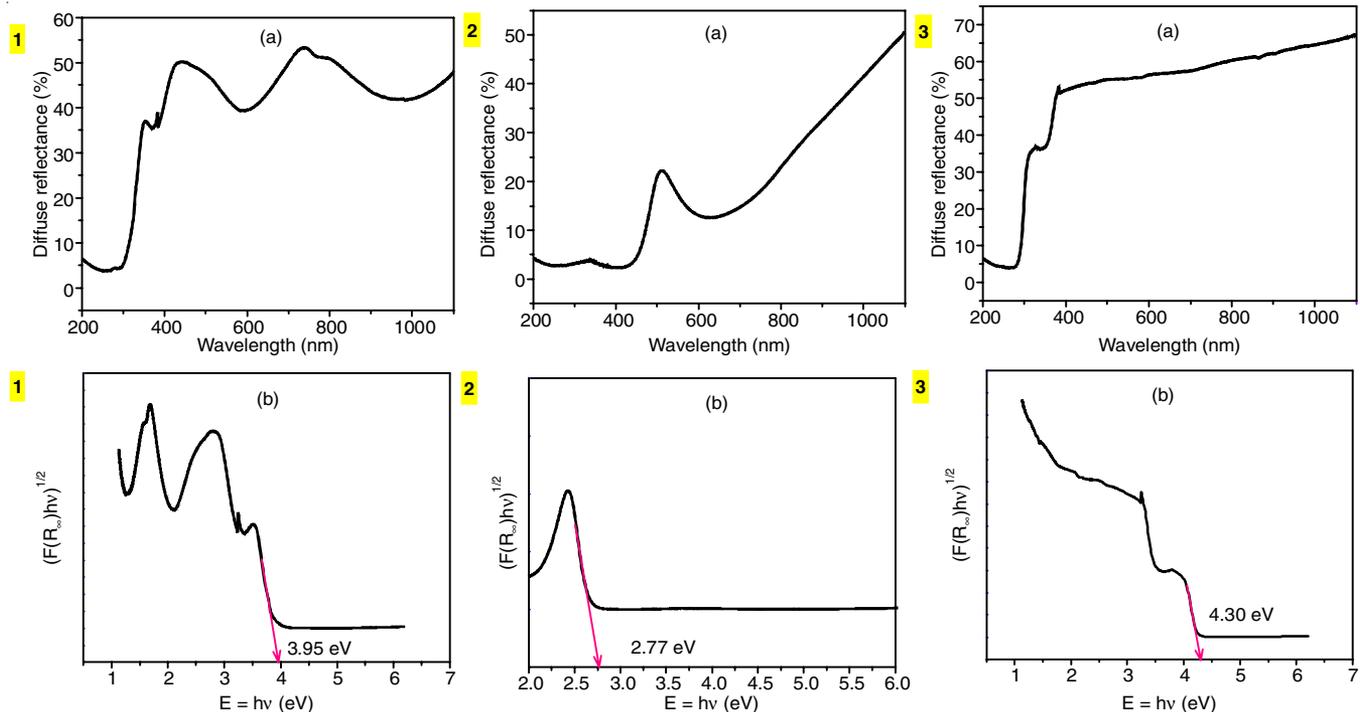


Fig. 1. (a) Diffuse reflectance spectra (b) Plots of $[F(R_{\infty})/hv]^{1/2}$ versus photon energy (hv) of the complexes 1, 2 and 3

Photoluminescence spectra: Photoluminescence excitation and emission spectra of the complexes 1-3 recorded at

room temperature are depicted in Fig. 2a and 2b, respectively. The excitation spectrum of complex 1 at 575 nm emission

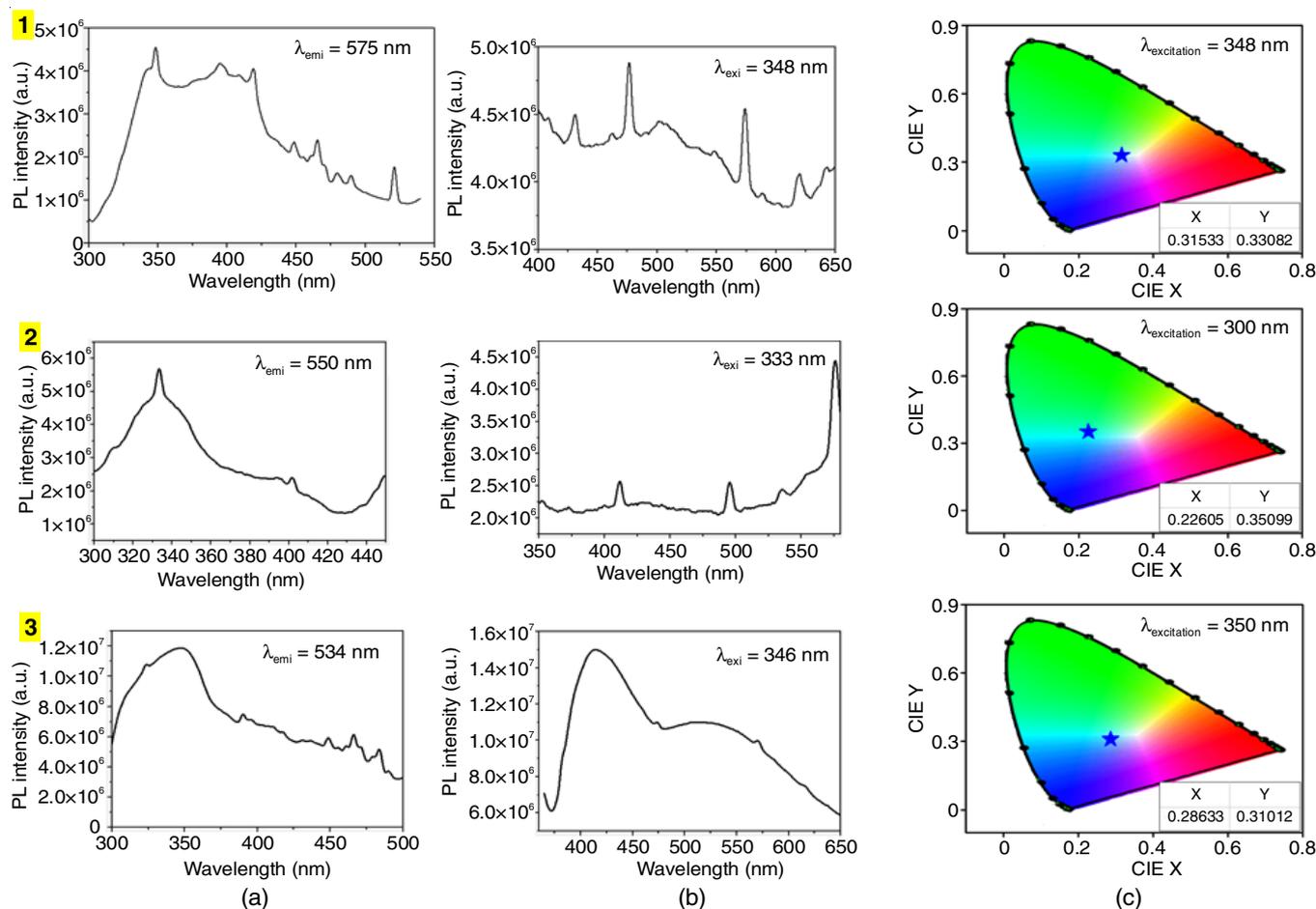


Fig. 2. Photoluminescence spectra of the complexes: (a) Excitation spectra, (b) Emission spectra, (c) CIE graphs of complexes (1), (2) and (3)

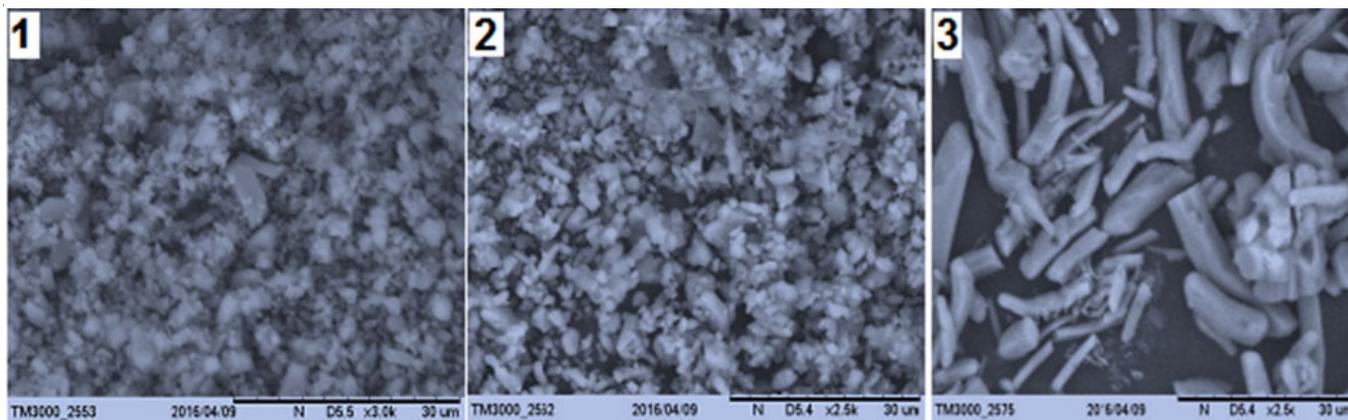


Fig. 3. SEM images of the complexes 1, 2 and 3

showed major excitations at 348, 395 and 448 nm. Similarly, the excitation spectrum of complex 2 ($\lambda_{\text{emi}} = 550$ nm) exhibited major peaks at 333 and 401 nm and for complex 3 ($\lambda_{\text{emi}} = 534$ nm), excitation peaks were found at 347, 390 and 448 nm. The PL spectra of the complexes indicated that these phosphors could effectively be excited by UV LED chip (360–400 nm). Commission International De I-Eclairage (CIE) 1931 chromaticity coordinates [30,31] for complexes 1, 2 and 3 were calculated for excitation wavelength respectively at 348, 300 and 350 nm. The estimated CIE coordinates (X and Y values) of complexes 1-3 are shown in the right corner of Fig.2c. The solid star circle sign used to represent the location of colour coordinates in the CIE chromaticity diagram indicated the colour of the complexes. From Fig. 2c graphs, one could observe that the colour of the complexes 1, 2 and 3 were found to be blue, green and white, respectively.

SEM analysis: The different surface morphologies and the arrangement of molecules for the synthesized complexes were evident from the SEM images (Fig. 3). Complex 1 showed spherical shaped particles, whereas nearly spherical shaped structures were observed for the complex 2. A smooth surface with stick like (length of 30 μm and breadth of 5 μm) morphology for the complex 3 was found visible. Earlier reports [32,33] revealed that materials made of inorganic complexes containing organic ligands with similar morphology and with varied particle size demonstrated better photoluminescence properties.

Conclusion

From the present work, it was concluded that the transition metal complexes involving pyridine and thiocyanate ligands could be synthesized by the direct reaction of metal salts with pyridine and ammonium thiocyanate in aqueous medium. For the synthesized complexes, which were primarily confirmed by the change in colour, melting points, IR and CHNS analysis were done. Phosphors 1-3 with a reasonably good band gap facilitate the processing of an emissive layer under ambient conditions and can become economically cheaper alternatives to conventional light emitting materials. The CIE graphs showed that the phosphors 1 and 3 could well be employed for white light emitting diodes and the phosphor 2 for green light emitting diodes. The photophysical properties studied using diffused reflectance and photoluminescence spectra substantiate that

these complexes could become promising emissive layers in OLEDs.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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