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Synthesis and Characterization of a New Aluminium Complex Bis (5-choloro-8-hydroxyquinoline)(2,2'bipyridine) Aluminium Al(Bpy)(5-Clq)$_2$

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We have synthesized a new aluminium complex, Bis (5-choloro-8-hydroxyquinoline) (2,2'bipyridine) aluminium Al(Bpy)(5-Clq)$_2$ and characterized it for structural, thermal and photoluminescence properties. The prepared material was characterized by Fourier-transformed infra-red spectroscopy (FTIR), thermal gravimetric analysis (TGA) and photoluminescence. The prepared material showed thermal stability up to 370 °C. Absorption Spectra of the material was measured by UV-visible spectroscopy. Solution of Al(Bpy)(5-Clq)$_2$ in ethanol showed peak at 393 nm, which may be attributed due to (π– π^*) transitions. The photoluminescence spectrum of Al(Bpy)(5-Clq)$_2$ in ethanol solution showed peak at 535 nm. The time resolved photoluminescence spectra of the material showed two life time components. The decay times of the first and second component are 5.3 ns and 21.2 ns respectively. The prepared material emits the light in green region (PL spectra) so it can be used as an emissive layer in organic light emitting diodes.

Keywords: Organometallic compounds, Chemical synthesis, Thermal stability, Photoluminescence spectroscopy, Time resolved spectroscopy.

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1. INTRODUCTION

In the past years, organic light-emitting diodes (OLEDs) have attracted great attentions in industrial and academic fields due to their potential of applications such as full-color, large-area, flat panel, flexible, and transparent displays as well as solid state lighting. OLEDs based display offers light weight devices with low power consumption compared with liquid crystal displays [1-2]. The fast response and wide viewing angle are also be printed over different type of substrates and this promises low cost fabrication and flexible devices [3-5]. Recently the main attention has been attracted on the application of metal complexes as electroluminescent materials for organic light emitting diodes (OLED) [6-9]. Organic light emitting diodes (OLEDs) are a recent area of interest for many research groups. Alq$_3$ is an organometallic molecule, which is widely used as an electron transport layer as well as a light emitting layer in organic LEDs because Alq$_3$ is a one of the most stable and fluorescent solid state material with excellent electron transport mobilities. It has also been used as a host for fluorescent and phosphorescent dyes [10-15]. In Alq$_3$ molecule blue to green luminescence can be tuned through the addition of substitutional groups [16-17]. A large number of organic materials have been synthesized and much efforts have been made to obtain high performance devices. [18-21]. But it is observed that electron transport mobility of the Alq$_3$ molecule is lower than the hole transport mobilities of the 4, 4'-bis [N-(1-Naphthyl)-N-Phenyl amino] biphenyl (NPB) and N,N'-diphenyl-N,N'-bis(1-naphtylphenyl)-1, 1'biphenyl-4, 4'-diamine (α-NPD) [22-23]. It is desired that to make high performance devices there is urgent need to develop photoluminescent materials having good electron mobility as well as good luminescence. The derivatives of Alq$_3$ has been synthesized by various groups [24-29]. In this work a new photoluminescent material Bis[5-choloro-8-hydroxyquinoline] [2,2'bipyridine] aluminium Al(Bpy)(5-Clq)$_2$ has been synthesized and characterized for its structural properties (FTIR, Mass spectroscopy), thermal stability (TGA), and optical properties (photoluminescence, UV-visible-spectra).

2. EXPERIMENTAL

2.1 Materials

High quality (Purity >99%) 5-choloro-8-hydroxyquinoline and 2,2'bipyridine were purchased from Sigma Aldrich (United states) . Aluminium nitrate nonahydrate [$Al(NO_3)_3.9H_2O$](Purity > 99 %) and ethanol (C_2H_5OH) (Purity ≥ 99 %) were purchased from Merck (Germany).

2.2 Synthesis of Material and Methods

The aluminium (III) complex was prepared by adding a solution of aluminium nitrate nonahydrate (1mmol) (375.134 mg) in 6ml of water to a solution of the ligands (1mmol) (156.19 mg) of 2,2'bipyridine [$C_{10}H_8N_2$] and 5-Choloro 8-hydroxyquinoline [C_9H_6ClNO] (2 mmol) (359.20 mg) in 60 ml of ethanol and pH was adjusted to neutral by adding ammonia solution. After stirring the mixture for 2h at 90 °C on a magnetic stirrer a yellowish colour precipitate was formed. The precipitate was washed with deionised water to remove the excess metal ions and then recrystallized with absolute ethanol to obtain Bis (5-choloro-8-hydroxyquinoline) (2,2'bipyridine) aluminium (III). The material was dried at 90 °C in a vacuum oven. The schematic diagram of Al(Bpy)(5-Clq)$_2$ synthesis is shown in Fig. 1.

The infrared absorption spectrum of the aluminium complex Al(Bpy)(5-Clq)$_2$ studied using a Nicolet 5700 spectrometer in the range of 1600 cm^{-1} to 500 cm^{-1}. Mass spectroscopy measurement of the aluminium

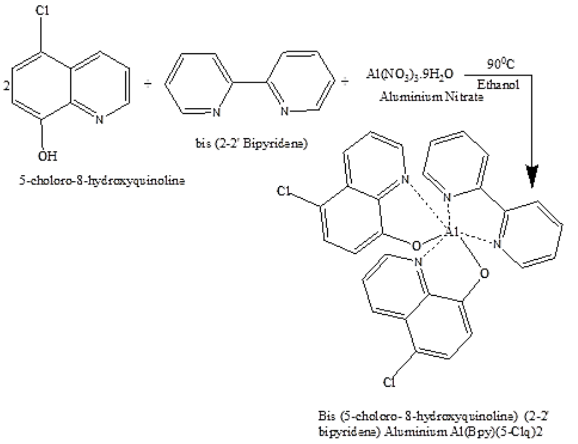

Fig. 1 – Synthesis of Bis (5-choloro- 8-hydroxyquinoline) (2,2'bipyridine) aluminium Al(Bpy)(5-Clq)$_2$

complex Al(Bpy)(5-Clq)$_2$ was done using Q-Tof micromass spectrometer. Elemental analysis of the aluminium complex Al(Bpy)(5-Clq)$_2$ was carried out on a Perkin Elmer elemental analyzer (400 CHN). Thermogravimetric analysis of the aluminium complex Al(Bpy)(5-Clq)$_2$ was done by using SDTA 851Metter-Toledo-star system in the temperature range from 20 °C to 500 °C. The UV-visible absorption spectra of the synthesized aluminum complex Al(Bpy)(5-Clq)$_2$ were recorded on a Shimadzu UV-2401 spectrophotometer. The photoluminescence spectra of the aluminium complex Al(Bpy)(5-Clq)$_2$ were recorded using a Fluorolog spectrofluorometer (Jobin yvon- Horiba model -3-11) at room temperature. Time-resolved PL decay spectra of the aluminium complex Al(Bpy)(5-Clq)$_2$ were recorded by a time-correlated single-photon counting (TCSPC) system from IBH (UK). During the experiment, the excitation wavelength and repetition rate were 341 nm and 1 μHz, respectively.

3. RESULTS AND DISCUSSIONS

3.1 Structural and Thermal Characterization of Material

The FTIR spectra of the aluminium complex Al(Bpy)(5-Clq)$_2$ was recorded in the range of 1600 cm^{-1} to 500 cm^{-1} as shown in Fig. 2. The peaks at 1503 and 1466 cm^{-1} is assigned to skeletal vibrational stretching of the aromatic ring. The vibrations at 1380 and 1328 cm^{-1} are due to C=C/C=N stretching in the quinoline fragments of Al(Bpy)(5-Clq)$_2$. The band at 1572 cm^{-1} are assigned to C=C stretching vibration involving quinoline ligand. Peaks at 756,781 and 827 cm^{-1} are due to quinoline group. Peak at 965 cm^{-1} might be attributed to trans double bond. Peak at 1040 cm^{-1} is characteristic of vibration of C-H group in aromatic ring located between two substituents. Peak at 606 cm^{-1} is observed due to metal-nitrogen bond. Additionally the band at 641 cm^{-1} arose due to stretching of the Al-O bond. FTIR analysis confirmed that the aluminium metal is well connected with polymer host. In mass spectrum fragment M/Z = 570 is corresponds to Al(Bpy)(5-Clq)$_2$. In mass spectrum peak at 570 correspond to molecular ion peak which confirmed the formation of the aluminium complex Al(Bpy)(5-Clq)$_2$. The CHN analysis of the complex indicated the formula to be Al (Bpy)(5-Clq)$_2$ (Found: C, 63.71; H, 4.73; N, 10.13; Calc.: C, 63.17; H, 4.24; N, 9.82; %). Thermo-gravimetric analysis (TGA) of the aluminum complex Al(Bpy)(5-Clq)$_2$ was done in the temperature range from 20 °C to 500 °C as shown in Fig. 3. The heating rate was 10 °C/min during the experiment. This aluminium complex Al(Bpy)(5-Clq)$_2$ shows thermal stability up to 370 °C. Above 370 °C, the aluminium complex exhibits a drastic weight loss. This might be ascribed to the decomposition of the polymeric host.

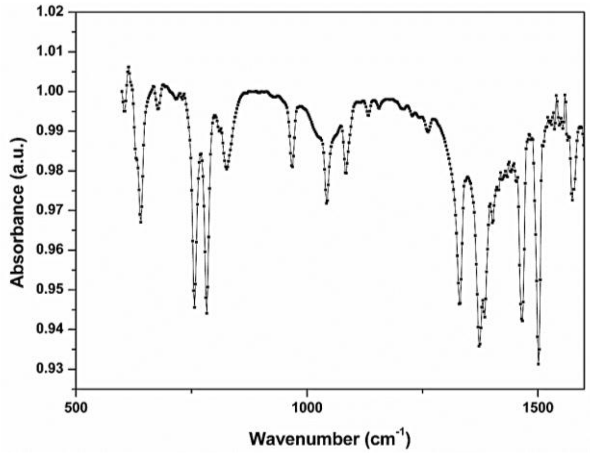

Fig. 2 – FTIR spectra of Bis (5-choloro- 8- hydroxyquinoline) (2,2'bipyridine) aluminium Al(Bpy)(5-Clq)$_2$

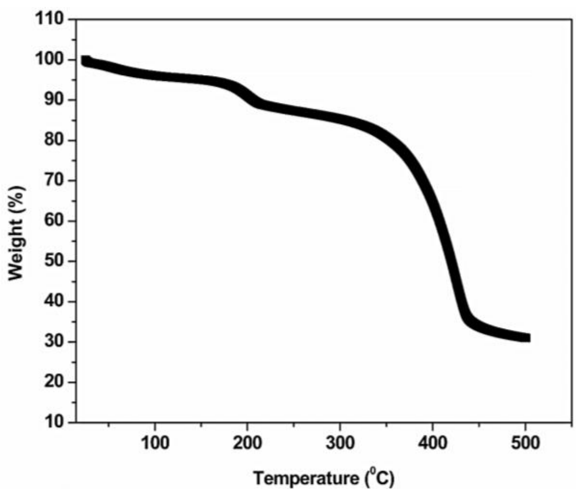

Fig. 3 – Thermo gravimetric analysis of Bis (5-choloro-8-hydroxyquinoline) (2,2'bipyridine) aluminium Al(Bpy)(5-Clq)$_2$

3.2 Spectral Characterization of the Material

The photoluminescence and UV-visible spectra were obtained in a solution of ethanol as shown in Fig. 4. The absorption spectra of this material shows maxima at 393 nm. It may be attributed to $\pi - \pi^*$ transition of the aromatic rings. Photoluminescence spectra for this material showed the most intense peak at 535 nm, which is consistent with the absorption spectra.

Photoluminescence spectra confirms that the prepared photoluminescent material emits the green light. The time resolved PL spectrum is shown in Fig. 5. Decay curve has two components. The curve is fitted by

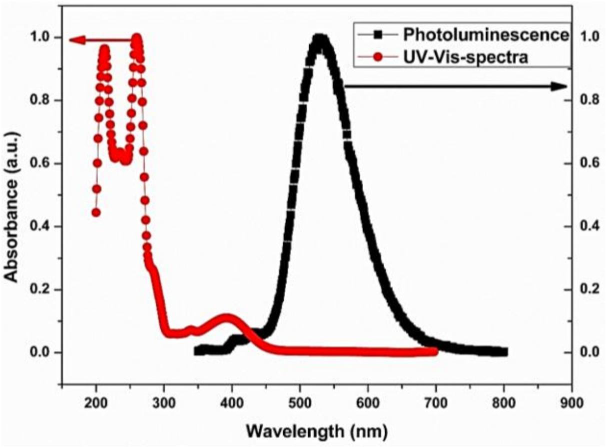

Fig. 4 – UV-visible and Photoluminescence spectra of Bis (5-choloro-8-hydroxyquinoline) (2,2'bipyridine) aluminium Al(Bpy)(5-Clq)$_2$

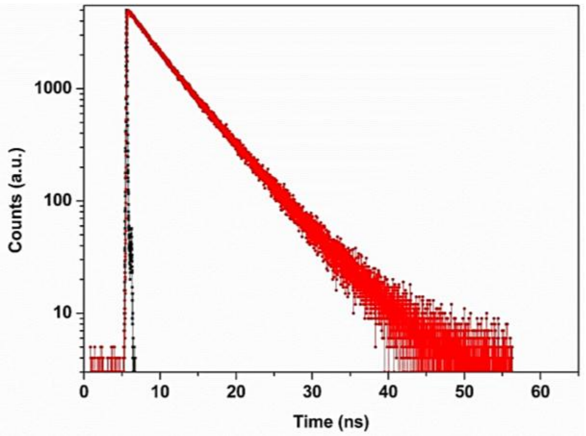

Fig. 5 – Time decay curve of Bis (5-choloro-8-hydroxyquinoline) (2,2'bipyridine) aluminium Al(Bpy)(5-Clq)$_2$

$I = a_1 e^{-t/\tau 1} + a_2 e^{-t/\tau 2}$, where τ_1 and τ_2 are the lifetime of the components with amplitude a_1 and a_2 [30].

The decay times of the first and second component are 5.3 ns and 21.2 ns respectively. The bi-exponential behaviour of the decay curve can be explained by a) a fast process which might be attributed to relaxation of the carriers into the unoccupied ground state, b) the slow process can be correlated with radiative recombination from the excited state. However, both the processes contribute to the energy transfer rate which depends on the acceptor concentration. The decay curve also indicates that the triplet energy transfer is completely suppressed in the aluminium complex [30-31].

4. CONCLUSION

A new photoluminescent material Al(Bpy)(5-Clq)$_2$ was fabricated with the reaction of (5-Choloro-8-hydroxyquinoline) and (2,2'bipyridine) with aluminium nitrate. This material shows thermal stability up to 370 °C. Material Al(Bpy)(5-Clq)$_2$ showed two life time components, 5.3 ns and 21.2 ns respectively. Photolumninescent material emits the green light in PL spectra. This material can be used as an emissive layer in organic light emitting diodes (OLEDs).

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