

# Synthesis and characterisation of blue organic electroluminescent bis (2-methyl 8-quinolinolato) (triphenyl siloxy) aluminium for OLEDs applications<sup>1</sup>

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## ABSTRACT

In the development of full color displays, based on OLEDs the emissions of different wavelengths are required. We synthesized a blue organic electroluminescent material bis (2 methyl 8- quinolinolato) (triphenyl siloxy) aluminum (III) (SAIq) and its electrical and optical properties were studied. The material exhibited high photoluminescence (PL) and electroluminescence (EL). Photoluminescence (PL) spectra recorded at room temperature revealed a broad blue emission peak at 490 nm along with a shoulder at 448 nm. The material was characterized by UV-visible, photoluminescence, electroluminescence and IR spectroscopic methods. The Thermo Gravimetric Analysis (TGA) revealed that the material is thermally stable upto 300 °C. From the absorbance cutoff wavelength at 410 nm and Tauc relation, the optical band gap of the material was evaluated to be 3.1 eV. OLEDs were fabricated in ITO/TPD/SAIq/LiF/Al configuration. The devices show typical non-linear diode I-V characteristics under forward bias with the threshold voltage of 5V. The CIE chromaticity was also studied and the coordinates were found to be independent of operating voltage.

## 1. INTRODUCTION

Since the first report on highly efficient organic light emitting diodes (OLEDs) by Tang and Van Slyke [1], they have attracted much interest for their potential application in flat panel displays. The performance of OLEDs has improved drastically during the last decade, through focused research efforts [2-10]. To achieve high quantum yield in electroluminescence of the organic layer and to get a balanced charge injection, many fluorescent dyes and charge transport materials have been developed. Using some very efficient dyes the energy of the incident light of a shorter wavelength can be converted into a longer one. Using proper dyes, blue light can be converted into green or red. In another way, a blue OLED alone has the potential to generate all the colors, while the converse: conversion of green or red emission into blue, by the same method is not possible [26, 27]. Efforts are going on in the area of colour tuning by molecular engineering, especially to achieve blue-light emission [11,12]. However, blue light emitters in general have lower efficiencies than green or red emitters, because of their larger band gap energy, which inhibits injection of electrons at cathode. Using the phosphorescent organometallic dyes the EL efficiency can tremendously be enhanced. FIrpic is the most popular blue emitting phosphorescent dye. Although all three principal colors have been demonstrated in OLEDs, but only green and orange OLEDs currently have the abilities to meet the requirements for commercial applications. Blue light-emitting diodes are still under development for commercial use. A number of comprehensive reviews on blue organic electroluminescent materials are available [13,14].

Many complexes of 8-hydroxyquinoline such as Alq<sub>3</sub>, Znq<sub>2</sub>, Mgq<sub>2</sub>, Znmq<sub>2</sub> and Beq<sub>2</sub> have been studied as emitters by many researchers [1,15,16]. In this report we have synthesized another 8-hydroxyquinoline derivative bis (2-methyl 8-quinolinolato)(triphenyl siloxy) aluminium (SAIq). Thin films of SAIq were deposited by the thermal evaporation in vacuum. These films were studied for their UV-visible optical absorption, luminescence, and infrared spectroscopic properties. The band gap of the material was determined from the optical absorption measurements. SAIq has been studied previously as hole blocking layers [17] and blue emitting host in the white emitting devices [18-20]. In this report we have studied SAIq as self-blue light emitter for OLED applications. Electroluminescent devices were fabricated in the bilayer TPD/SAIq configuration.

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## 2. EXPERIMENTAL AND DEVICE FABRICATION

The 8-hydroxyquinoline derivative bis (2 methyl 8- quinolinolato) (triphenyl siloxy) aluminium (SAIq) was synthesized through a homogenous-phase reaction of 2-methyl 8-quinolinol (2 mole) with aluminum iso-propoxide (1 mole) and triphenyl silanol (1 mole) at room temperature [20]. The product was filtered and dried for 1h at 90 °C under vacuum and further purified by vacuum sublimation at a reduced pressure of about  $5 \times 10^{-5}$  Torr. The resultant SAIq was obtained as a white powder. The chemical structure of SAIq is shown in Fig. 1. Devices were fabricated on the ITO substrate by a vacuum deposition method. The indium tin oxide (ITO) coated glass substrates with a sheet resistance of  $20 \Omega/\square$ , were patterned by photolithographic technique and were cleaned following a chemical cleaning process with soap solution, followed by boiling in trichloroethylene and isopropyl alcohol and finally dried under vacuum. The devices were fabricated in the configuration ITO/TPD(25nm)/SAIq(35 nm)/LiF(3 nm)/Al(150 nm). The thermal evaporation of organic materials was carried out in a diffusion pumped chamber at a base pressure of  $1 \times 10^{-5}$  Torr. The hole transport layer (TPD) and emissive layer (SAIq) were deposited at a rate of  $1\text{-}2 \text{ \AA s}^{-1}$ , the thin buffer layer of LiF (3 nm) was deposited at the rate of  $\sim 0.3 \text{ \AA s}^{-1}$ , while Al was evaporated at the rate of  $10 \text{ \AA s}^{-1}$ . The thickness of all the thin films was measured using a HINDHIAC quartz crystal thickness monitor DTM –101. After fabrication, the device was transferred to a glove box, which resulted in a brief exposure of the device to air. The device was hermetically sealed in the glove box under dry nitrogen atmosphere and then was taken out. Subsequently, all the electrical measurements were done in the ambient atmosphere. Fig. 2 shows the device configuration. The current vs voltage characteristics were studied using a Keithley 617 electrometer interfaced with a PC.

## 3. RESULT AND DISCUSSION

The UV- visible absorption spectra of the vacuum deposited SAIq thin film (300 nm) on quartz substrate were studied in the wavelength region 200-800 nm using a Shimadzu UV-2401 PC spectrophotometer at room temperature (Fig. 3). The absorption maximum occurs at 260 nm with a shoulder at 358 nm and the cutoff wavelength at 410 nm. The optical band gap was determined from the optical absorption edge and using the Tauc relation [21, 22]

$$Ah\nu = (h\nu - E_g)^n \quad (1)$$

where  $n$  is 1/2 for allowed direct, 2 for allowed indirect, 3/2 for forbidden direct and 3 for forbidden indirect transitions materials,  $A$  is the absorbance,  $E_g$  is the band gap corresponding to a particular absorption occurring in the film, and  $h\nu$  is the photon energy. The direct optical band gap for SAIq,  $E_g$  was obtained from extrapolation of the straight-line portion of the Absorbance<sup>2</sup> vs  $h\nu$  plot to  $A = 0$  (Fig. 4) as 3.1 eV.

SAIq showed bright blue photoluminescence when illuminated by a 400 nm light source. The photoluminescence (PL) and electroluminescence (EL) spectra of SAIq are shown in Fig.3. The PL and EL were recorded by using HR 2000 Ocean Optics Spectrometer, having a CCD array and fiber optic probe. The optical transition responsible for the PL is due to a transition from the electron rich phenoxide ring (location of the highest occupied molecular orbital, HOMO) to the electron deficient pyridyl ring (location of the lowest unoccupied molecular orbital, LUMO) [23]. The electron-hole recombination taking place in the emitting layer leads to the emission of a blue light with a maximum at  $\lambda_{\text{max}} = 490 \text{ nm}$ , which is 40 nm shorter than that of  $\text{Alq}_3$ . It has been reported that in  $\text{Mq}_3$  complexes ( $M = \text{Al, Ga, In}$ ) the 8-hydroxyquinoline works as a bidentate ligand and form chelate complexes with the central metals [24]. It is well known fact that as the co-valent nature of the metal-nitrogen bonding in  $\text{Mq}_3$  complex is decreased, emission shifts to shorter wavelength [16, 25]. In SAIq the blue shift can be attributed due to the reduction in the chelation of the complex compared to  $\text{Alq}_3$ .

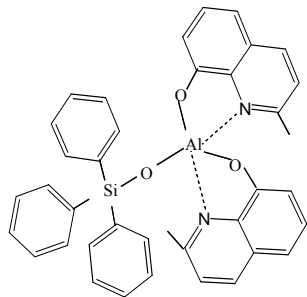


Fig. 1. Bis (2methyl-8-quinolinolato)(triphenylsiloxy)

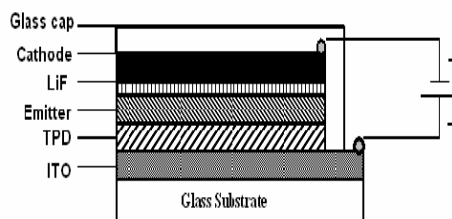


Fig. 2. Multilayer configuration of Organic Light Emitting Diode.

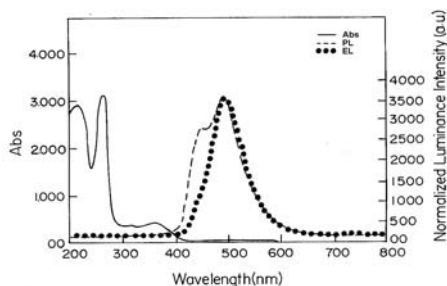


Fig.3 Absorbance, photoluminescence and electroluminescence spectra of SALq.

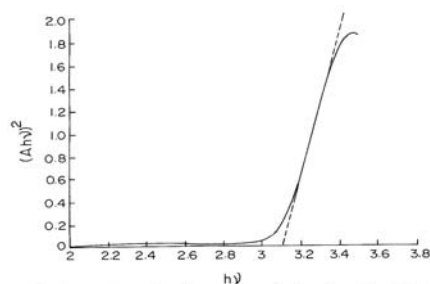


Fig.4 Absorbance<sup>2</sup> vs photon energy ( $h\nu$ ) extrapolated to zero absorbance for the determination of band gap energy of SALq

The perfect match of EL with the PL spectra at 490 nm indicates that the same excited species (singlet excitons) are responsible for both processes. The exciton energy, determined as  $E_{ex}$  (eV) =  $1240/\lambda_{max}$  (nm) = 2.5 eV and the optical band gap  $E_g = 3.1$  eV, determined from the optical absorbance (Fig.3) suggest the exciton binding energy [22] to be  $E_{bind} = E_g - E_{ex} \sim 0.60$  eV. An important observation has been made that the electroluminescence (EL) peak position and the CIE coordinates of the device are independent of the operating voltage. The EL emission stayed at 490 nm (Fig.5) and the CIE chromaticity coordinates stayed at (0.11, 0.19).

The thermal stability of the complex was determined by Thermo Gravimetric Analysis (TGA). Fig. 6 shows the TGA and its first derivative curves for SALq. It was recorded on a Mettler TA 3000 System at a scan rate of 10 °C/min under nitrogen atmosphere. It is clear from the curve that the complex is thermally stable upto 300 °C and the maximum weight loss occurs at about 455 °C.

Fig. 7 shows the current vs voltage characteristic of the EL device under forward bias. The forward bias current was obtained when the ITO was a positive electrode and the Al as negative one. The characteristic shows highly non-linear nature with ohmic conduction at low voltages and trap limited conduction at high voltages. The current and luminescence increased steeply with the forward bias voltage. The current rises steeply above 5V indicating the onset of light emission. The emission was uniform over the entire active area of the device pixel.

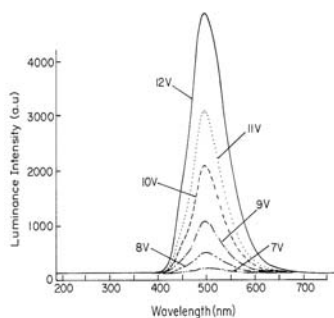


Fig.5 Electroluminescence characteristics of ITO/TPD/SALq/LiF/Al device at different voltages

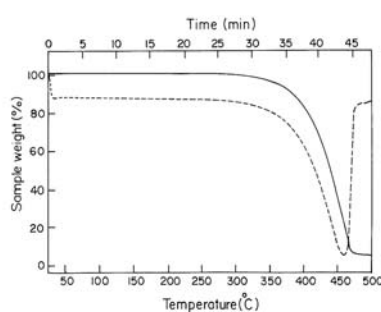


Fig.6 TGA curve (solid) and its first derivative (dotted) of SALq at the rate of 10°C/min under N<sub>2</sub> purging

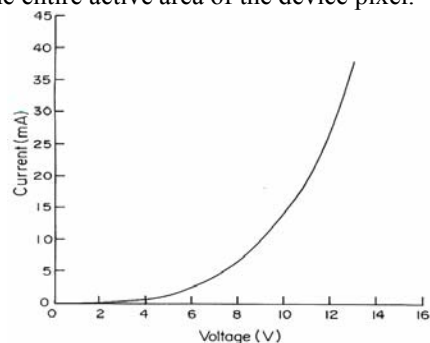


Fig.7 IV characteristic of ITO/TDP/SALq/LiF/Al device (active area 4mm<sup>2</sup>)

## 4. CONCLUSION

We have synthesized an aluminum complex SALq and used it as an emitter in organic LED devices. It exhibits good thermal stability upto 300°C. The position of PL and EL peaks at the same wavelength (490 nm) indicates the involvement of the singlet exciton in both the processes. Also the chromaticity of the device was found to be independent of the operating voltage and it shows the typical diode characteristics in forward bias. The results confirm that SALq could be used as an emissive source for OLED applications.

## REFERENCES

- [1] C. W. Tang and S. A. VanSlyke "Organic electroluminescent diode" *Appl. Phys. Lett.* Vol. 51, pp. 913-915, 1987.
- [2] J. H. Burroughes, D. D. Bradley, A. R. Brown, R. N. Marks, K. Machay, R. H. Friend, P. L. Burns and A. B. Holmes, "Light-emitting diodes based on conjugated polymers" *Nature* vol. 347, pp. 539-541, 1990.
- [3] Y. Yang, Q. Pei and A. J. Heeger, "Efficient blue polymer light-emitting diodes from a series of soluble poly(paraphenylene)s" *J. Appl. Phys.* vol. 79, pp. 934-939, January 1996.
- [4] A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu and E. P. Woo, "High brightness and efficiency blue light-emitting polymer diodes" *Appl. Phys. Lett.* vol. 73, pp. 629-631, August 1998.
- [5] J. Kido and T. Matsumoto, "Bright organic electroluminescent devices having a metal-doped electron-injecting layer" *Appl. Phys. Lett* vol. 73, pp. 2866-2868, November 1998.

- [6] J. Stampfl, S. Tasch, G. Leising and U. Scherf, "Quantum Efficiencies of Electroluminescent Poly(Para-Phenylenes)" *Synth. Met.* vol. 71, pp. 2125-2128, 1995.
- [7] L. Kumar, S. K. Dhawan, M. N. Kamalasanan and S. Chandra, "Bright-orange organic light emitting diodes fabricated using benzene-naphthalene co-polymer" *Thin Solid Films* vol. 441, pp. 243-247, 2003.
- [8] X. D. Feng, R. Khangura and Z.H. Lu, "Metal-organic-metal cathode for high-contrast organic light-emitting diodes" *Appl. Phys. Lett.* vol. 85, pp. 497-499, July 2004.
- [9] T. H. Chen, Y. Liou, T. J. Wu and J. Y. Chen, "Enhancement of organic light-emitting device performances with Hf-doped indium tin oxide anodes" *Appl. Phys. Lett.* vol. 85, pp. 2092-2094, September 2004.
- [10] R. Paetzold, K. Heuser, D. Henseler, S. Roeger, G. Wittmann and A. Winnacker, "Performance of flexible polymeric light-emitting diodes under bending conditions" *Appl. Phys. Lett.* vol. 82, pp. 3342-3344, May 2003.
- [11] J. P. J. Markham, E. B. Namdas, T. D. Anthopoulos, I. D. W. Samuel, G. J. Richards and P. L. Burn, "Tuning of emission color for blue dendrimer blend light-emitting diodes" *Appl. Phys. Lett.* vol. 85, pp. 1463-1465, August 2004.
- [12] L. Kumar, R. R. Koireng, A. Misra, P. Kumar, S. K. Dhawan, M. N. Kamalasanan and S. Chandra, *Phys. Pure and Appl.* vol. 43, pp. 56- January 2005.
- [13] A. Misra, L. Kumar, P. Kumar, S. K. Dhawan, M. N. Kamalasanan and S. Chandra, "Blue electroluminescence in organic semiconductors" *Indian J. Pure and Appl. Phys.* vol. 42, pp. 793-805, November 2004.
- [14] D. Y. Kim, H. N. Cho and C. Y. Kim, *Prog. Polym. Sci.* vol. 25, pp. 1089, 2000.
- [15] Y. Hamada, T. Sano, M. Fujita and Y. Nishio, "Organic Electroluminescent Devices with 8-Hydroxyquinoline Derivative-Metal Complexes as an Emitter" *Jpn. J. Appl. Phys.* vol. 32, pp. L514-L515, April 1993.
- [16] C. H. Chen and J. Shi, *Coord. Chem. Rev.* vol. 171, pp. 161, 1998.
- [17] Y. Sato, S. Ichinosawa, T. Ogata, M. Fugono and Y. Murata, "Solid state characterization and x-ray crystal structure of a 1:1 complex of tetrathiafulvalene and *meta*-dinitrobenzene (TTF-*m*DNB)" *Synth. Met.* vol. 111, pp. 25-28, 2000.
- [18] Y. Sato, T. Ogata, S. Ichinosawa and Y. Murata, "Characteristics of organic electroluminescent devices with new dopants" *Synth. Met.* vol. 91, pp. 103-107, 1997.
- [19] J. T. Lim, M. J. Lee, N. H. Lee, Y. J. Ahm, C. H. Lee and D. H. Hwang, "Efficient white light emitting devices with a blue emitting layer doped with a red dye" *Curr. Appl. Phys.* vol. 4, pp. 327-330, 2004.
- [20] Y. W. Ko, C. H. Chung, J. H. Lee, Y. H. Kim, C. Y. Sohn, B. C. Kim, C. S. Hwang, Y. H. Song, J. Lim, Y. J. Ahn, G. W. Kang, N. Lee and C. Lee, "Efficient white organic light emission by single emitting layer" *Thin Solid Films* vol. 426, pp. 246-249, 2003.
- [21] J. Tauc, R. Grigorovici and A. Vancu, *Phys. Stat. Sol.* vol. 15, pp. 627, 1966.
- [22] I. Seguy, P. Jolinat, P. Destruel, J. Farence, R. Many, H. Bock, J. Ip and T. P. Nguyen, "Red organic light emitting device made from triphenylene hexaester and perylene tetraester" *J. Appl. Phys.* vol. 89, pp. 5442-5448, May 2001.
- [23] A. Curioni and W. Andreoni, *IBM J Res. and Dev.* vol. 45, pp. 101, 2001.
- [24] P. E. Burrow, Z. Shen, V. Bolovic, D. M. McCarty, S. R. Forrest, Cronin, M. E. Thompson, "Relationship between electroluminescence and current transport in organic heterojunction light-emitting devices" *J. Appl. Phys.* vol. 79, pp. 7991-8006, May 1996.
- [25] T. A. Hopkins et al *Chem. Mater.* vol. 8, pp. 344, 1996.
- [26] L. J. Rothberg and A. J. Lovinger, *J. Mater. Res.* vol. 11, pp. 3174, 1996.
- [27] T. Virgili, D. G. Lidzey and D. D. C. Bradley, "Efficient Energy Transfer from Blue to Red in Tetraphenylporphyrin-Doped Poly(9,9-dioctylfluorene) Light-Emitting Diodes" *Adv. Mater.* vol. 12, pp. 58, January 2000.