Improvement in the environmental stability of tris(8-hydroxyquinoline) aluminum by substitution of sulphonic acid in 8-hydroxyquinoline ligand

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Tris (8-hydroxyquinoline) aluminum (Alq_3) is a commonly used electron transporting and/or light emitting material in organic light emitting diodes (OLEDs). However, it is well known that Alq_3 is very sensitive to atmosphere exposure and that photoluminescence of Alq_3 films decreases with the time of atmosphere exposure. Degradation is also a serious problem in Alq_3 based OLEDs. Several degradation mechanisms have been identified in these devices, including formation of unstable cationic species due to passage of holes. Therefore, there is lots of interest in improving the stability of Alq_3. We have synthesized Tris (8-hydroxyquinoline-5 sulphonic acid) aluminum ($Al(qS)_3$) in order to improve the stability. We performed electron spin resonance measurements on Alq_3 and $Al(qS)_3$ powders. Unlike Alq_3 which exhibited strong ESR signal, $Al(qS)_3$ produced no detectable ESR signal indicating absence of free radicals in this material. To test the environmental stability of $Al(qS)_3$ films, we have performed photoluminescence (PL) measurements in humid air at different temperatures and found that $Al(qS)_3$ exhibits improved stability. After comparing the stability of Alq_3 and $Al(qS)_3$ thin films, fabrication of the light emitting diodes with $Al(qS)_3$ emitting layer was attempted in order to compare the performance with Alq_3 based devices.

1. INTRODUCTION

Alq_3-based organic light emitting diodes, OLEDs [1], have been developed into prototypes for commercial purposes, but their reliability still remains a challenging issue. One of the problems with organic LEDs, both low molecular and polymer based, is that they degrade rapidly during operation [2], and premature failure remains problematic in view of consumer uses. It has been found that tris (8-hydroxyquinoline)-aluminum (Alq_3) is very sensitive to atmospheric moisture and oxygen, which produce nonemissive species acting as luminescence quenchers [3,4]. Degradation has been attributed to various mechanisms, including crystallization of the organic layers, electrochemical reactions at the electrode/organic interface, migration of ionic species, and electrochemical reactions. Moreover, the ambient atmosphere shows strong influence on the characteristics of electrical devices like field effect transistors (FETs) or OLEDs, and on the electronic structures of Alq_3 films, whereas oxygen alone seems to have a smaller effect [5, 6].

The properties of an emitting material, such as luminescence yield and intrinsic stability, can be changed by modifying the localized electron states involved in the luminescence process. This can be achieved by specific chemical substitutions on the quinolate rings. The electron-donor substituents generally destabilize the π electronic states of aromatic systems, and this effect decreases with increasing distance from the substituents. On the other hand, electron acceptor substituents stabilize the π electronic states of aromatic systems, and this effect also decreases with increasing distance from the substituents. Therefore, a substitution on the phenoxide ring will act mainly on the HOMO set, where as a substitution on the pyridyl ring will act mainly on the LUMO set [7]. As a result the electronic states at a higher energy than the LUMOs and those at a lower energy of the HOMOs are delocalized on both rings of the quinolate

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ligands, the optimum substitution strategy is to put an electron-acceptor group on the phenoxide ring (enhancing the mixing of the HOMOs with the states at lower energy) and/or an electron donor group on the pyridyl ring (enhancing the mixing of the LUMOs with the states at higher energy). Moreover, owing to both electronic and structural factors, the most suitable positions for the chemical substitution are positions 4 and 5 on the quinolate ligand, namely those "para" to the oxygen atom and the nitrogen atom [7].

In the present work, the new compound tris(8-hydroxyquinoline-5-sulfonic acid) aluminum ($Al(qS)_3$) has been synthesized by chemical route and the elementary analysis (CHN) has been done. The ESR spectrum was recorded to check the presence of free radicals. The emission and excitation spectra have been measured on the spectrofluorometer. Influence of external factors, such as humid air, on luminescence has been studied at different temperatures. All the results have been compared with Alq_3. Finally, preparation of OLEDs with $Al(qS)_3$ as emitting species was attempted in order to compare their performance to Alq_3 based devices.

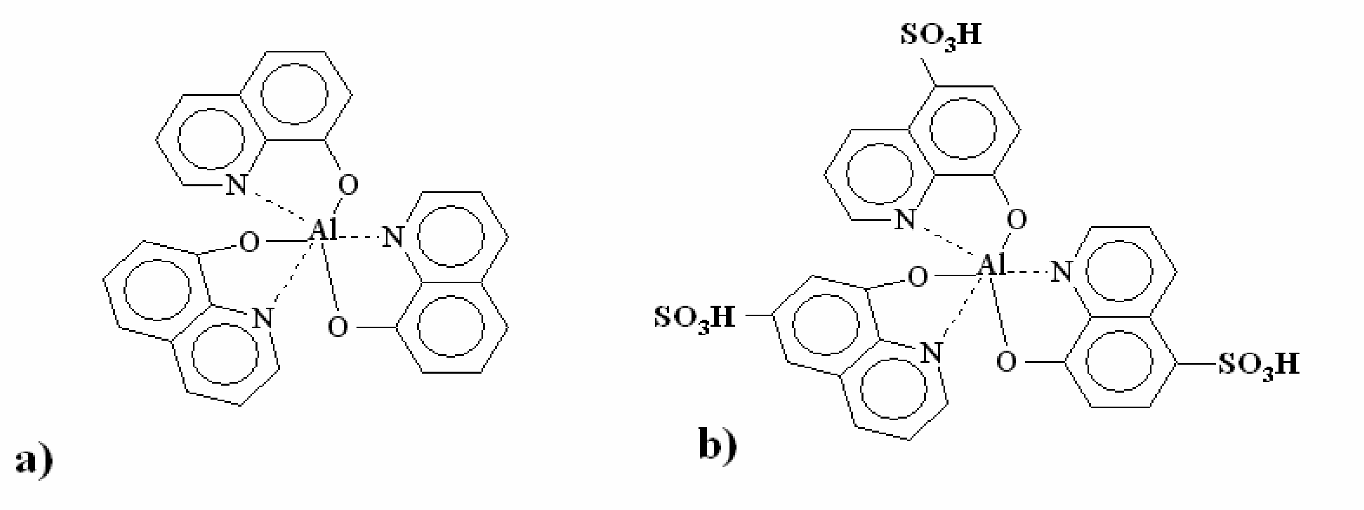

Figure 1 Chemical structures of a) Alq_3 and b) $Al(qS)_3$

2. EXPERIMENTAL DETAILS

$Al(qS)_3$was prepared as follows: 1.46 gm (6 mmol) of 8 - hydroxy quinoline-5-sulfonic acid (8HqS) was dissolved in 30 ml of de-ionized water and heated up to 80 ^oC to get clear solution and filtered to remove insoluble impurities. Then 0.75 gm (2 mmol) of $Al(NO_3)_3.9H_2O$ was dissolved in 100 ml of de-ionized water. This solution was also warmed to 50 ^oC for 30 minutes. Later the heated (80 ^oC) 8 - hydroxy quinoline-5-sulfonic acid solution was slowly added to Al $(NO_3)_3.9H_2O$ solution. The final product was washed with de-ionized water till the filtered water becomes colourless. Finally, Aluminum tris (8 - hydroxy quinoline-5-sulfonic acid) was dried at 60 ^oC for two hours in order to remove water molecules. The maximum yield of powder is 1.05 gm. From the elementary analysis, 46.35 % C, 2.58 % H, 6.01 % N and 27.47 % O were observed. The structure of the compound is given in figure 1. To study the stability of the powder material, $Al(qS)_3$, ESR measurements were carried out on a Varian E-112 E-line Century Series Spectrometer working in the microwave X-band and Bruker EMX EPR Spectrometer. Then, thin films of $Al(qS)_3$were spin coated on glass substrates for PL studies. Since the attempt to purify $Al(qS)_3$ material by train sublimation was unsuccessful ($Al(qS)_3$ failed to sublime), spincoating instead of thermal evaporation needs to be used. Alq_3 films were prepared by thermal evaporation. Photoluminescence spectra of these thin films were measured by means of a conventional spectrofluorometer Spex Fluorolog-3.

For device fabrication thin films of poly(vinyl alcohol) (PVA) doped with $Al(qS)_3$ (5% loading) were spincoated on cleaned ITO substrates from N, N-dimethylformamide (DMF) and methanol solutions. $Al(qS)_3$ showed the best solubility in dimethyl sulfoxide (DMSO), but spincoating from DMSO resulted in very thin poor quality films. The ITO substrates were cleaned with the following cleaning procedure: first rinsed by ethanol, acetone, toluene, then acetone, ethanol, and DI water. After that, the substrates were cleaned in ultrasonic bath for 10 minutes in acetone, ethanol, and

DI water respectively, and dried in an oven. After drying, UV ozone treatment was performed by exposing the substrates to a 20W UV light source (wavelength 254 nm) with 12 cm distance under oxygen flow. The luminance-current-voltage characteristics were measured using Keithley 2400 sourcemeter and Oriel MS 260I monochromator with integrating sphere and CCD detector.

3. RESULTS AND DISCUSSION

Free radicals are compounds with uncoupled electrons in valence orbitals which are inherently unstable. The free radicals inherently present in organic materials try to stabilize themselves, i.e. to complete their atomic orbitals, by reacting with the hydrogen of other organic compounds, R-H, as in the following:

$$\mathrm{In}\cdot + \mathrm{R{-}H} = \mathrm{In{-}H} + \mathrm{R}\cdot \tag{1}$$

Where In· represents the radical form of a generic initiator, In-H is now a stable compound and R· is a new radical, which is unstable like In· was before the reaction. The radical R· can then proceed to react like in (1) and the original organic compound R-H is going to be completely destroyed in due time. This degradation process is known to happen in organic compounds, and it depends on the initial products and on the physical and chemical conditions in the environment. In this regard, presence of oxygen can play a significant role. Indeed, O_2 is a diradical molecule because of its triplet ground state and, as such, reacts very quickly with any radical as follows:

$$\mathrm{R}\cdot + \mathrm{O_2} = \mathrm{R{-}O{-}O}\cdot \tag{2}$$

where R-O-O· is a much more active radical than R· thus reacting still more:

$$\mathrm{R{-}O{-}O}\cdot + \mathrm{R{-}H} = \mathrm{R{-}O{-}O{-}H} + \mathrm{R}\cdot \tag{3}$$

and so on until the total destruction of the original stable organic compound R-H. In practice, presence of O_2 can accelerate the degradation of the material, a process which is commonly called auto-oxidation. This phenomenon likely contributes to the degradation of Alq_3 and other organic emitting materials.

It is known that uncoupled electron states or free radicals or chemical initiators, can already exist in the pristine organic compounds. Recently, it has been proposed that the presence of free radicals is mainly responsible for Alq_3 degradation [9]. Such intrinsic degradation is different from other known degradation mechanisms such as thermally induced degradation including morphological or crystallization of amorphous organic thin films, electrochemically or charge-induced degradation, and interfacial degradation. The presence of free radicals and hence the stability of the material is verified by recording ESR (Electron Spin Resonance) measurements. In organic molecule, the ESR signal is produced either by uncoupled electron states, i.e. free radicals, or by paramagnetic impurities in the starting materials. ESR signal due to polarons was reported in conjugated electroluminescent polymers [9]. Free electrons are another possible source of ESR signal, but their contribution should not be significant in a material with such relatively low conductivity as Alq_3. Figure 2 shows the ESR spectra of Alq_3 and $Al(qS)_3$. While broad ESR signal can be observed for Alq_3, no signal is obtained for $Al(qS)_3$. where there is no such broad ESR signal observed for $Al(qS)_3$ as like Alq_3. Therefore, the above results clearly indicates the absence of free radicals in $Al(qS)_3$. The absence of free radicals in $Al(qS)_3$ and presence in Alq_3 indicates the enhanced stability of $Al(qS)_3$ as compared to Alq_3.

The photoluminescence (PL) spectrum was observed in a conventional spectro-fluorometer, Spectro-Fluorolog-3. Figure 3 shows the normalized photoluminescence spectrum of Alq_3 and $Al(qS)_3$ films obtained for 380 nm excitation. It can be observed that the emission spectrum of $Al(qS)_3$ is blue shifted for ~20 nm compared to Alq_3. Also, the FWHM of the emission from $Al(qS)_3$ is larger compared to FWHM of Alq_3. The blue shift in $Al(qS)_3$ is expected since the substitution of electron-withdrawing group at C5 or C7 position of the phenoxide side will cause the blue shift [10]. The obtained PL spectrum is in good agreement with recently reported PL spectrum of $Al(qS)_3$ in a solution [11]. However, it should be pointed out that the PL intensity of $Al(qS)_3$ film is lower than that of Alq_3. The reasons for reduction in PL intensity are not fully clear. Similar phenomenon can be observed in some commercially available Alq_3 derivatives such as tris(5,7-dichloro-8-hydroxyquinolinato)-aluminium.

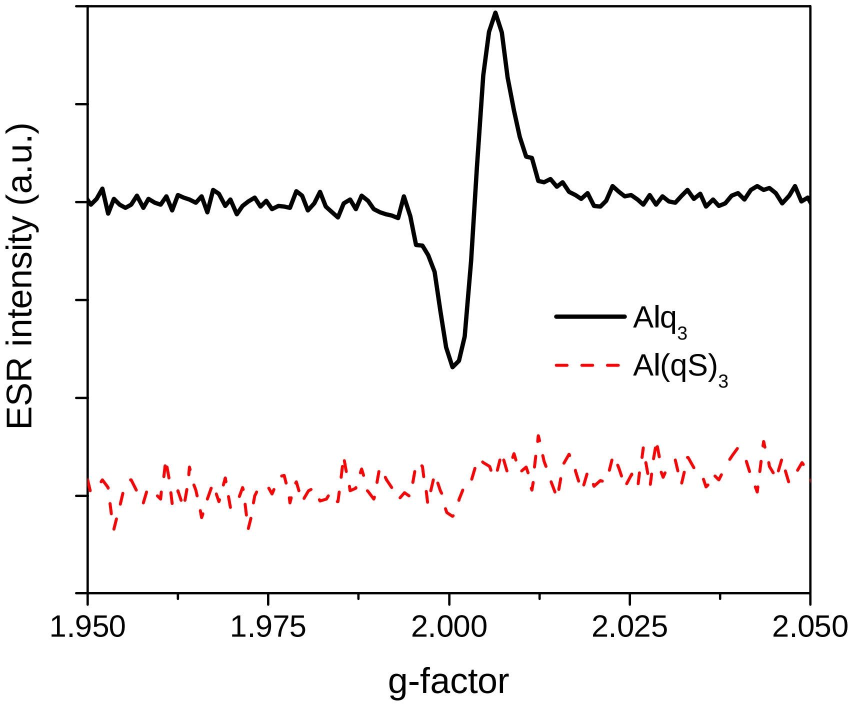

Figure 2: The ESR signal observed at room temperature of as synthesized Alq$_3$ powder and as synthesized Al(qS)$_3$ powder.

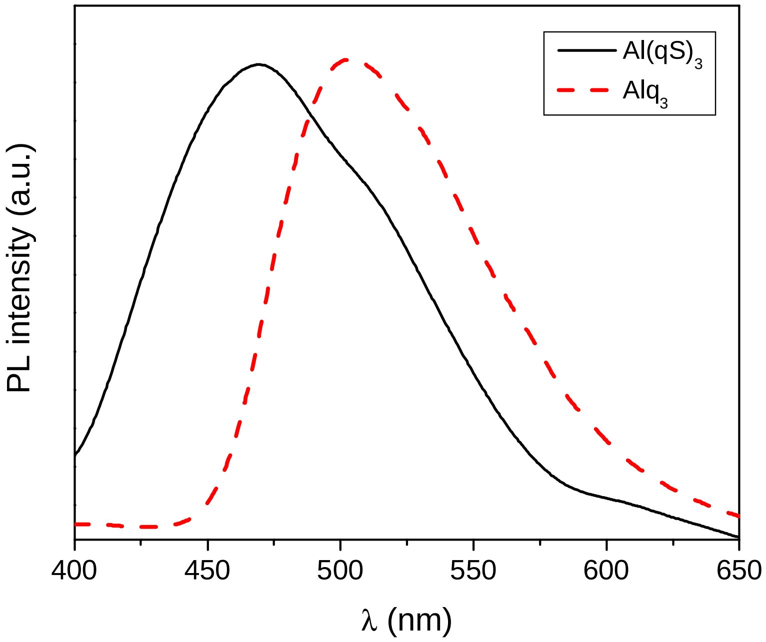

Figure 3 Comparison between photoluminescence of Al(qS)$_3$ and Alq$_3$. Excitation wavelength is 380 nm.

The fluorescence lifetimes of a substance usually represents the average amount of time the molecule remains in the excited state prior to its return to the ground state. Lifetime measurements are frequently necessary in fluorescence spectroscopy. These data can reveal the frequency of collisional encounters with quenching agents, the rate of energy transfer and the rate of excited state reactions. Moreover, calculations of rotational correlation times from fluorescence anisotropies require knowledge of the fluorescence lifetime. The precise nature of the fluorescence decay can reveal details about the interactions of the fluorophore with its environment. For example, multiple decay constants can be a result of a fluorophore being in several distinct environments, or a result of different excited state processes.

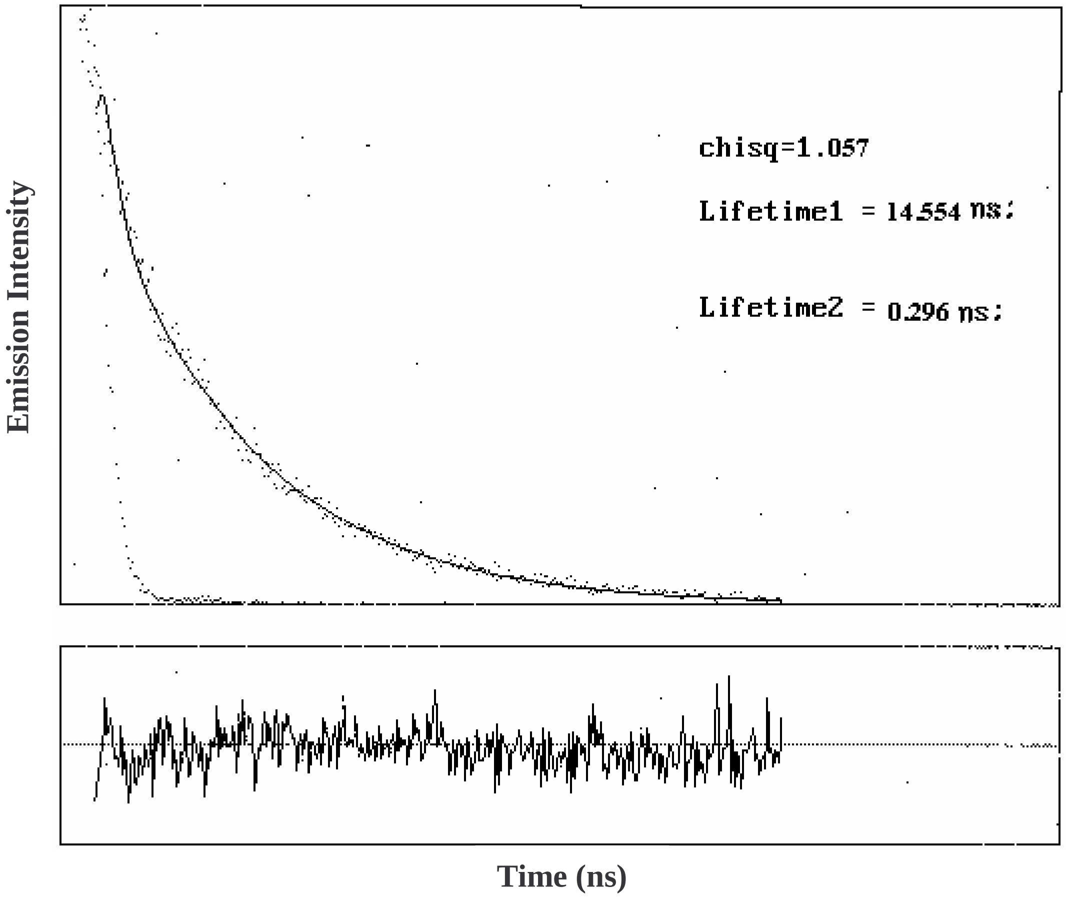

Figure 4: Emission and excitation spectra for time resolved decay measurement for Al(qS)$_3$

To investigate the excited state mechanisms, the luminescent decay experiments were performed for aluminum tris (8-hydroxy quinoline-5-sulfonic acid) film using FL900CDT fluorescence life time spectrometer. The obtained experimental data was fitted by a single exponential curve for aluminum tris (8 - hydroxy quinoline-5-sulfonic acid) film with the decay time of $\tau = 14$ ns at RT as shown in the Figure 4. The fitting error for the curve is also given below the graph. The above mentioned decay time, 14 ns, is similar with Alq$_3$ decay time that is 16.4 ns [12], indicating that the same singlet to singlet transitions take place in Al(qS)$_3$.

It is well known that organic compounds are more susceptible to detrimental effects of oxygen and moisture. To study the effects of these parameters, following experiments were performed. A stainless steel enclosure fixed with a copper plate at the bottom for heating the sample was used. The top of the chamber is provided with one inlet which allows the gases and the other outlet is for maintaining the pressure. For the annealing in humid air, the atmospheric air was allowed to pass through the inlet which was immersed in water of the conical flask and the outlet was connected with the inlet of the stainless steal chamber. The thin film of sample Alq$_3$ was annealed in humid air environment at various temperatures for 15 minutes, starting from 50 ^{o}C. In order to avoid errors in measurement the sample was heated at the same place every time inside the enclosure. Then the sample was transferred to spectrofluorometer compartment for photoluminescent emission measurements. The normalized emission maximum intensity is plotted as function of annealing temperature. The intensity of the emission is almost same up to 170 °C decreases very fast beyond 170 °C, and disappears almost completely at 240 °C as shown in figure 5 (curve b). There was a small recovery of photoluminescent emission observed around 130 °C.

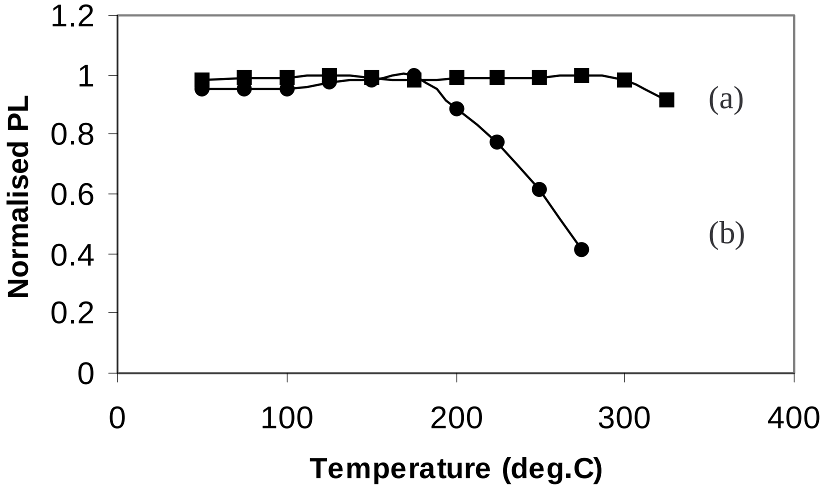

Figure 5: Variation in photoluminescent emission for (a) Al(qS)$_3$ and (b) Alq$_3$ in annealing temperature at humid air environment, excited at 390 nm

It is known that the annealing at different temperatures can significantly affect the properties of Alq$_3$ including the PL emission. In recent years, different crystalline phases of Alq$_3$ by thermal sublimation process in vacuum and a strong blue shift of the photoluminescence maximum have been reported by Brutting and co-workers [13, 14]. Previous study of photoluminescence of Alq$_3$ films [4] observed decay of PL signal with atmospheric exposure and proposed likely chemical reactions causing this deterioration. Papadimitrakopoulos *et al.* [4] demonstrated that the PL intensity reduces with annealing of Alq$_3$ film at 175°C, which is slightly above the glass transition temperature of Alq$_3$. This is in agreement with the results obtained here. Therefore, the loss of emission beyond 170 °C can be attributed to the phase transition since the glass transition temperature of Alq$_3$ is ~172°C [4].

The same set of experiments were repeated for the new material Al(qS)$_3$, to know the environmental stability of the material as shown in the figure 3 (curve a). It was found that Al(qS)$_3$ is comparatively more stable than Alq$_3$ because the PL output is almost constant till 270 °C which is higher than that of the Alq$_3$ (cut-off temperature, 170 °C). The some loss of emission was observed beyond 270 °C and attributed to the some morphological changes in film, which has also been verified by DSC measurements (Differential Scanning Calorimetry) for Al(qS)$_3$ powder sample which occurs at 272 °C. Since, there is no abrupt change in the PL emission till sufficiently higher annealing temperature, Al(qS)$_3$ exhibits improved environmental stability compared to Alq$_3$. However, the PL intensity is also reduced compared to Alq$_3$.

After demonstrating improved environmental stability of Al(qS)$_3$ films and powders, we fabricated an OLED with Al(qS)$_3$ as emitting material. Since Al(qS)$_3$ does not readily evaporate, the devices were fabricated by spincoating. After drying the film, Al electrode was evaporated. The current-voltage characteristics is shown in Fig. 6. The devices spincoated from DMF and methanol solutions showed similar performance, though current density at low voltages was larger in the device prepared from methanol solution. The devices show blue emission around 9-10V, which is initially intense but then quickly drops to barely measurable levels and remains about the same with further increase of the driving voltage. Due to different device structure and fabrication methods, direct comparison with Alq$_3$ based devices is not possible. It should be noted that Al(qS)$_3$ based devices show relatively large current density for such a simple device structure. Luminescent yield is inferior compared to Alq$_3$, though there is a possibility that it can be improved by more complex device structure and different choice of host polymer. Even if luminescent yield cannot be substantially increased, Al(qS)$_3$ represents an excellent candidate for an electron transport material since very large current densities at relatively low driving voltage can be achieved.

In general, metal complexes based on substituted 8-hydroxyquinoline likely represent a good alternative to conventionally used Alq_3. Depending on the nature (electron-withdrawing vs. electron-accepting) and the position of the substituent, both blue and red shifts can be achieved, while in some cases it is possible to improve the stability. Stability and efficiency, however, will be different for different derivatives.

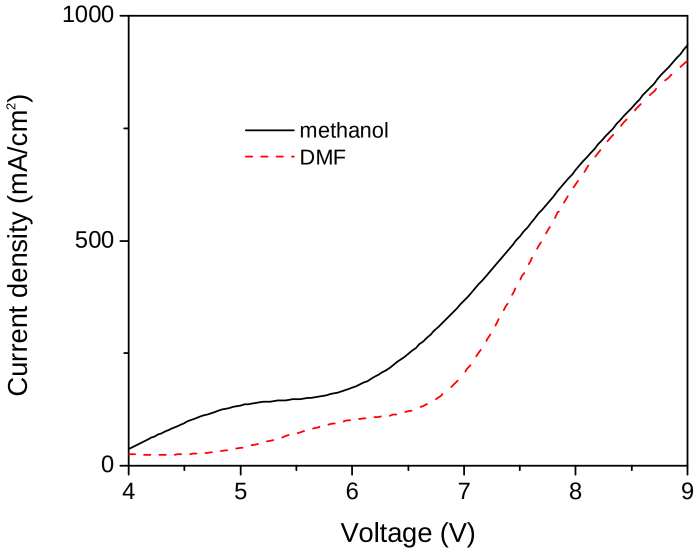

Figure 6 a) Current vs. voltage for ITO/PVA:Al(qS)$_3$/Al devices.

4. CONCLUSION

We have synthesized Tris (8-Hydroxyquinoline -5- Sulphonic acid) Aluminum in attempt to improve environmental stability of a commonly used emitting material Tris (8-Hydroxyquinoline) Aluminum. It was found that the new material, $Al(qS)_3$, is thermally and environmentally more stable than Alq_3. The stability of the material in the powder form was verified by ESR measurements. While in Alq_3 broad ESR peak is obtained, no signal is detected in $Al(qS)_3$. The environmental stability of the films was verified by annealing the thin films of both Alq_3 and $Al(qS)_3$ in humid air and the corresponding photoluminescence (PL) study shows that $Al(qS)_3$ is comparatively more stable than Alq_3 because the PL decreases in the humid air was noticed beyond 270 ^oC which is higher than that of an abrupt change in Alq_3 which is at 170 ^oC. The emission peak of $Al(qS)_3$ exhibits ~20nm blue shift, which is expected from substitution of the electron-withdrawing group at position 5 in the phenoxide ring of the quinoline ligand. The OLED devices with PVA:$Al(qS)_3$ emission layer exhibited large current density at low voltage but low luminescence. It is expected that luminescence can be improved in more complex device structures.

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