



ORIGINAL ARTICLE

Synthesis and photophysical properties of aluminium tris-(4-morpholine-8-hydroxyquinoline)



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Abstract Aluminium tris(4-morpholinyl-8-hydroxyquinoline) has been synthesized and characterized. The photoluminescence measurements showed that the new derivative is blue shifted and has relative photoluminescence quantum yield two times higher compared to the pristine Al tris(8-hydroxyquinoline). Differential scanning calorimetric studies revealed that the newly synthesized Alq₃ derivative in this work is amorphous material with the highest transition glass temperature value among the reported amorphous Alq₃ derivatives.

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Introduction

Aluminium tris(8-hydroxyquinoline) is a widely used material in photovoltaic applications due to its excellent electronic and thermal properties. In organic light emitting diodes (OLEDs), it has been used successfully as electron transporting layer and/or emitting layer [1–6]. Recently, the use of the parent Alq₃ and its derivatives in organic solar cells (OSCs) as dopant and/or buffering layer has been reported to increase the efficiency and the life time of the cell [7–11].

Curioni and Andreoni [12] provided a clue for obtaining more efficient Alq₃ derivatives with enhanced intrinsic luminescence by attaching specific chemical substitutions on the

quinolate ligand. The study stated that the introduction of an electron donating group at 4-position will widen the band gap energy and cause a blue shifted emission maximum compared to the parent Alq₃ and the opposite is true for 5-position. Based on this study many research groups focused on the synthesis of new Alq₃ derivatives and studying their photoluminescence (PL) and electroluminescence (EL) properties.

In our previous efforts we have designed and prepared Alq₃ derivatives with different substitutions at C-4 and C-5 in order to achieve derivatives with better stability, higher efficiency and different emission colors [13,14]. Among the different prepared 4- and 5-substituted Alq₃ [13–17], derivatives with nitrogen functionalities at C-4 were proved to be exceptionally efficient emitters in OLEDs in addition to their efficiency in OSC when used as dopant [9,14].

On the other hand amorphous materials have received growing attention as materials for photovoltaic applications. Compared with crystalline materials, amorphous materials tend to form uniform, stable and transparent thin films during the OLED fabrication [18]. Transition glass temperature is a key factor that determines the thermal stability of amorphous material. The best of our knowledge, the blue shifted Alq₃

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derivative, Al tris(4-piperidin-1-yl-quinolin-8-ol), was the first reported amorphous AlQ_3 derivative with high transition glass temperature ($T_g = 196\text{ }^\circ\text{C}$), excellent photoluminescence, electroluminescence and thermal properties in addition to its improved solubility in organic solvents compared to the parent AlQ_3 [14].

Solvent free amination is environmentally friendly synthesis which offers high yield in short reaction time [19,20]. In previous work, we were able to prepare 4-piperidyl-8-hydroxyquinoline and 4-(4-methylpiperazinyl)-8-hydroxyquinoline in high yields (95% and 88%, respectively) by solvent free amination reaction [14]. The current study will focus on the preparation of a new amorphous 4-substituted AlQ_3 derivative through the synthesis of the new ligand 4-morpholinyl-8-hydroxyquinoline using solvent free amination reaction and complexing it to Al^{3+} . The synthesis is followed by spectroscopic and thermal studies in comparison to the parent AlQ_3 and other AlQ_3 derivatives.

Experimental

General

Melting points and T_g were determined using METTLER TOLEDO DSC 821 thermo analyzer. NMR (^1H and ^{13}C) analysis were performed on bruker DPX 200 (200 MHz) spectrometer using $\text{DMSO-}d_6$ solution referenced internally to Me_4Si , J values are given in Hz. TLC were performed on dry silica gel plates and developed by using chloroform/methanol mixture as eluent. The starting material 4-chloro-8-tosyloxyquinoline **1** has been prepared from the commercially available xanthonic acid according to the earlier reported procedures [21].

Synthesis of 4-morpholinyl-8-hydroxyquinoline (2)

4-Chloro-8-tosyloxyquinoline **1** (0.5 g, 1.5 mmol) was mixed with morpholine (1.4 mL, 16 mmol) and heated in an oil bath

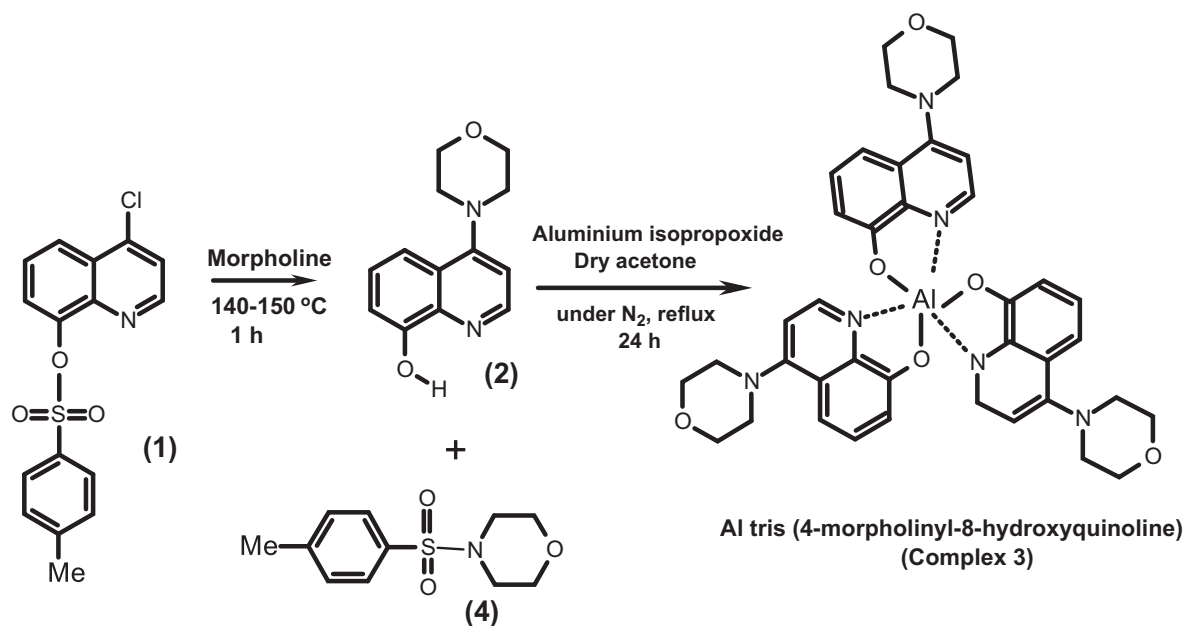
at $140\text{--}150\text{ }^\circ\text{C}$ for 1 h. After cooling to room temperature, water was added (15 mL). The formed precipitate was filtered, dissolved in hot ethanol (5 mL) and then allowed to cool. The formed colorless crystals was found to be 4-tosylmorpholine **4** (mp $146\text{--}7\text{ }^\circ\text{C}$, lit. $147\text{--}8\text{ }^\circ\text{C}$ [22,23]) which was separated by filtration and the filtrate was concentrated and allowed to cool. Then the title compound was separated as yellowish crystals (mp $131\text{--}2\text{ }^\circ\text{C}$, yield 0.31 g, 90%). ^1H NMR (200 MHz, $\text{DMSO-}d_6$) δ 3.18 (s br, 4H), 3.88 (s br, 4H), 7.02–7.07 (m, 2H), 7.35–7.49 (m, 2H), 8.66–8.69 (d, $J = 4.8\text{ Hz}$, 1H); ^{13}C NMR (50 MHz, $\text{DMSO-}d_6$) δ 52.5, 66.6, 109.8, 111.1, 114.0, 123.7, 126.7, 140.1, 148.89, 154.2, 156.7. HRMS ($M + H$) $^+$ calc for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_2$: 231.1134, found: 231.1131.

Synthesis of Al tris(4-morpholinyl-8-hydroxyquinoline) (3)

4-Morpholinyl-8-hydroxyquinoline **2** (0.20 g, 0.87 mmol) and Al isopropoxide (0.06 g, 0.29 mmol) were refluxed in dry acetone for 24 h under N_2 atmosphere. The reaction mixture was concentrated and petroleum ether was added. The title compound was separated as greenish yellow powder and dried in oven at $60\text{ }^\circ\text{C}$ (yield 0.27 g, 87%). ^1H NMR (200 MHz, $\text{DMSO-}d_6$) δ 3.26–3.36 (m, 12H), 3.81 (s br, 12H), 6.62–6.66 (d, $J = 7.6$, 1H), 6.72–7.13 (m, 9H), 7.32–7.42 (m, 3H), 8.34–8.37 (d, $J = 5.3$, 1H), 8.44–8.47 (d, $J = 5.3$, 1H). HRMS ($M + H$) $^+$ calc for $\text{C}_{39}\text{H}_{40}\text{N}_6\text{O}_6\text{Al}$: 715.2825, found: 715.2827.

DSC measurements

To detect the overall thermal properties of the new AlQ_3 derivative, 1 mg of complex **3** was heated from $25\text{ }^\circ\text{C}$ to $500\text{ }^\circ\text{C}$ by dynamic $20\text{ }^\circ\text{C}/\text{min}$ heating rate in a standard $40\text{ }\mu\text{g}$ Al cup with 60 ml/min N_2 flow. For determination of T_g , 5 mg of the new AlQ_3 derivative was heated from $-50\text{ }^\circ\text{C}$ to $350\text{ }^\circ\text{C}$ with $20\text{ }^\circ\text{C}/\text{min}$ heating rate and cooled back to $-50\text{ }^\circ\text{C}$. The procedure was repeated three times to remove the thermal history.



Scheme 1 The synthetic route for complex 3.

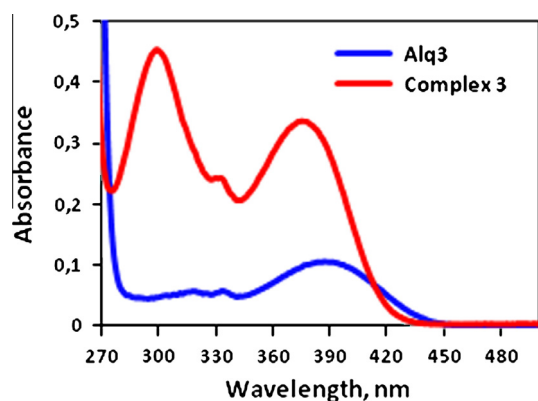


Fig. 1 Absorption spectra of Alq₃ and complex 3.

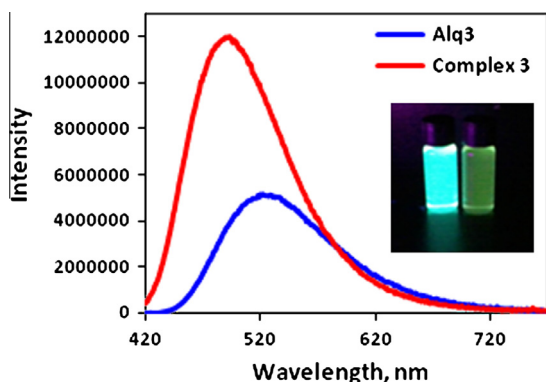


Fig. 2 The PL emission spectra of Alq₃ and complex 3, the inserted photo is for Alq₃ (right, green) and complex 3 (left, bluish) under UV light.

Results and discussion

Synthesis and characterization

4-Morpholinyl-8-hydroxyquinoline **2** has been prepared under solvent free condition by reacting 4-chloro-8-tosyloxyquinoline **1** [21] with morpholine at 140–150 °C. ¹H NMR analysis of the product revealed that the product is a mixture of **2** and 4-tosylmorpholine **4**. The two products were then separated depending on their relative solubility in ethanol. The formation of the ligand **2** was proved by ¹H NMR, ¹³C NMR spectroscopy and HRMS. The splitting of the tosyl protecting group during the amination reaction of 4-chloro-8-tosyloxyquinoline **1** was also observed during the amination of **1** with pyrrolidine and it was attributed to the high nucleophilicity of

the alicyclic mines [21]. The solvent free amination offered fast reaction with a high yield of **2** (90%).

Then ligand **2** was allowed to react with aluminium isopropoxide in refluxing acetone under N₂ atmosphere for 24 h. The formed Alq₃ derivative **3** was observed to be highly soluble in organic solvents such as alcohols and acetone compared to the parent Alq₃. ¹H NMR analysis for the new Alq₃ derivative **3** proved the formation of the meridional isomer which is more stable than the facial isomer [24]. The overall synthetic route for **3** is described in Scheme 1.

Absorption and photoluminescence properties of complex 3

UV–vis absorption spectrum of the new derivative **3** showed two absorption bands at 299 nm and 375 nm. The morpholinyl substituent at C-4 shortened the absorption wavelength of the new derivative compared to the parent Alq₃ Fig. 1. This proves that the morpholinyl substitution at C-4 is powerful enough to change the π–π* system effectively and widen the optical band gap.

The photophysical properties of the new Alq₃ derivative correlate well with the electronic properties of the morpholinyl group at C-4. The electron donating property of the morpholinyl group ($\sigma_p = -0.51$, calculated from pK_a value) caused a blue shift of 33 nm in the emission spectrum of the new derivative compared to the parent Alq₃ as shown in Fig. 2. Moreover, the relative fluorescence quantum yield (Φ_{PL}) of the new complex is two times higher than that of the parent Alq₃ as shown in Table 1. The optical band gap energy of the new Alq₃ derivative is higher than that of the parent Alq₃ in agreement with the blue shifted PL emission spectra. In comparison with the efficient emitter Al tris(4-piperidin-1-yl-quinolin-8-ol) ($\lambda_{PL} = 477$ nm, $\Phi_{PL} = 2.1$) [14], complex **3** is also blue shifted (489 nm) and has almost similar relative PL quantum yield value ($\Phi_{PL} = 2.02$). The UV–vis absorption and PL emission spectra in Figs. 1 and 2 were made in chloroform solution and the results are summarized in Table 1.

DSC measurements

The DSC thermogram of the new Alq₃ derivative **3** showed no melting endotherm up to 500 °C. However a glass transition endotherm was clearly observed at 232 °C Fig. 3. The absence of the melting endotherm during the measurement indicates that the complex is amorphous. In addition the higher transition glass temperature of complex **3** than the parent Alq₃ (T_g of Alq₃ = 174 °C) [26] indicates higher stability of the glass phase which increases device efficiency [18]. In the open literature, only four amorphous Alq₃ derivatives have been reported with various T_g values ranging from 142 to 216 °C [14,27],

Table 1 The photophysical and thermal properties of Alq₃ and complex 3.

Complex	$\lambda_{ab}(\epsilon)^a$	λ_{em}^b	Φ_{PL}^c	Optical band gap ^d	T_g (°C)
Alq ₃	387 (5.9×10^3)	522	1	3.19	174
3	375 (16.9×10^3)	489	2.02	3.31	232

^a Absorption maximum (nm) and molar absorptivity ($L \text{ mol}^{-1} \text{ cm}^{-1}$) in brackets.

^b Photoluminescence emission maximum (nm) of 20 μM of sample in chloroform.

^c Relative photoluminescence quantum yield with respect to Alq₃ giving a quantum yield of 1.00 to Alq₃ (the absolute quantum yield for Alq₃ in chloroform is 0.223 [25]).

^d Estimated from the UV–vis spectra by using $E = hc/\nu$.

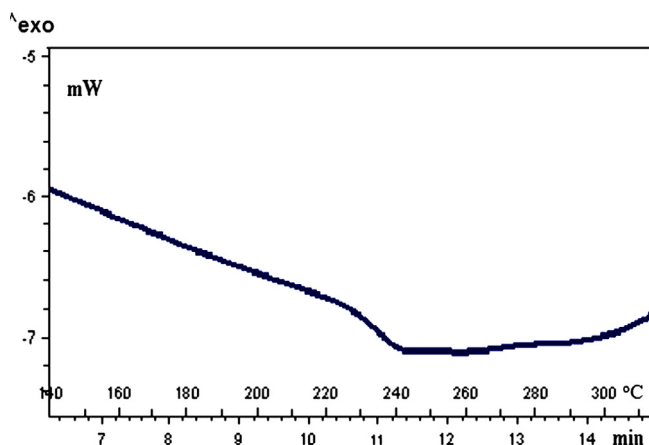


Fig. 3 Transition glass endothermic peak in the DSC thermogram of complex 3.

three of those amorphous derivatives have higher relative fluorescence quantum yield than the parent Alq_3 . It is also worth to mention that all the reported amorphous Alq_3 derivatives are amino substituted derivatives at C-4. The newly synthesized Alq_3 in this work (complex 3) has the highest T_g value so far ($T_g = 232^\circ\text{C}$). Generally complex 3 is expected to be the most thermally stable material of the new emerging generation of amorphous Alq_3 derivatives due to the absence of melting endotherm along with the highest T_g value.

Conclusion

A new ligand, 4-morpholinyl-8-hydroxyquinoline, could be prepared in a high yield by the reaction of 4-chloro-8-tosyloxyquinoline and morpholine under solvent free condition. The attachment of the saturated cyclic morpholinyl group at C-4 in the newly synthesized Alq_3 derivatives improved the thermal and photophysical properties compared to the parent Alq_3 . The new derivative showed blue shifted emission spectrum, excellent photoluminescence properties and higher relative photoluminescence quantum yield compared to the parent Alq_3 . DSC measurement revealed that complex 3 is amorphous with high transition glass temperature (232°C). The efficient PL properties, high solubility along with the amorphous property and high T_g value indicate that the newly synthesized Alq_3 derivative in this work can be employed as a highly efficient emitter in OLED devices.

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