



New Alq₃ derivatives with efficient photoluminescence and electroluminescence properties for organic light-emitting diodes

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ABSTRACT

Two new ligands prepared under solvent free conditions and five aluminum complexes derived from 8-hydroxyquinoline have been synthesized and characterized. The majority of the new aluminum tris(8-hydroxyquinoline) derivatives have nitrogen functionalities at position-4 of the quinolate ligand. The photoluminescence emission wavelengths of the new Alq₃ derivatives are shifted according to the electronic properties of the substituents at position-4. Results from differential scanning calorimetry (DSC) investigations of the new Alq₃ derivatives indicate that the complexes **9** and **10** are non crystalline and have higher transition glass temperatures than the parent Alq₃. The EL measurements of OLED devices with complexes **7**, **9**, and **10** as emitters revealed that complexes **7**, **9**, and **10** are efficient emitters in organic light emitting diodes.

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1. Introduction

Organic light emitting diodes are a recent area of interest for many research groups. OLED-based displays offer light weight devices with bright colors and low power consumption compared to liquid crystal displays. The fast response and wide viewing angle are also extra advantages for OLED based displays over the LC displays.^{1,2} OLEDs can also be printed over different types of substrates and this promises low cost fabrication and flexible displays.^{3,4}

Alq₃ is an organometallic molecule, which is widely used as an electron transport layer^{5,6} as well as a light emitting layer in organic LEDs,^{7–11} and it has also been used as a host for fluorescent and phosphorescent dyes.^{12,13}

Tuning the emission wavelength of Alq₃ through modulation of HOMO levels by synthesizing differently substituted 8-hydroxyquinolines in which the substitutions are introduced to the phenoxide ring¹⁴ (C-5, C-6, and C-7), has been the objective of various previous studies. Azenbacher and co-workers^{15–18} have produced 5-aryl and 5-ethynylaryl-8-hydroxyquinolines, in which their Alq₃ derivatives showed emission color tuning covering the whole visible spectrum, and a maximum external quantum efficiency of 0.90% could be detected in an OLED with Al tris[5-[2-(4,6-dimethoxy-1,3,5-triazinyl)-8-quinolate]. Armstrong and co-workers¹⁹ have introduced the strong electron withdrawing

–SO₂NR₂ group at C-5 of the 8-hydroxyquinoline and EL investigations of the resulting Alq₃ derivative revealed that the emission wavelength was significantly blue shifted (λ_{PL} =480 nm) compared with the emission wavelength of the parent Alq₃ (λ_{PL} =514 nm). 8-Hydroxyquinolines with alkoxymethyl, amino-methyl and carbazole substituents at C-5 have been also prepared and the photophysical properties of their Alq₃ derivatives have been studied.^{20–23}

Difluorinated Alq₃ derivatives in which the two fluorine atoms are introduced to the phenoxide ring at either C-5 and C-6 or C-6 and C-7 have also been considered as promising emitters based on theoretical investigations of the ionization potentials and electron affinities.²⁴

Although substitutions at position-4 of the quinolate ligand are specially favored sterically and electronically,¹⁴ 4-substituted Alq₃ derivatives for OLED applications are still rare. Tuning the emission of Alq₃ through the modulation of the LUMO levels, which are localized on the pyridyl side of the 8-hydroxyquinoline ligand (C-2, C-3, and C-4) has so far been the objective of only a few previous studies.^{25,26}

On the other hand, amorphous morphology and high transition glass temperature (T_g) are highly desired properties for materials used in organic light emitting devices. Compared with crystalline materials, amorphous materials are able to form more stable and uniform transparent thin films either by using vacuum deposition or spin coating.^{27–34} High T_g values of metal complexes often indicate high glass phase stability, which increases devices efficiencies^{35,36} as they are able to stand higher ambient temperatures.³¹

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In our present work we have focused on the design and synthesis of new Alq₃ derivatives, which can be used as efficient emitters in OLED devices. The two new 8-hydroxyquinoline ligands in this work are prepared in one-step and high yields by using solvent-free reactions between 4-chloro-8-hydroxyquinoline and the appropriate amine. The solvent free synthesis is preferred over the traditional synthesis because it offers short reaction time, high yields and it is environmentally friendly.^{37–41}

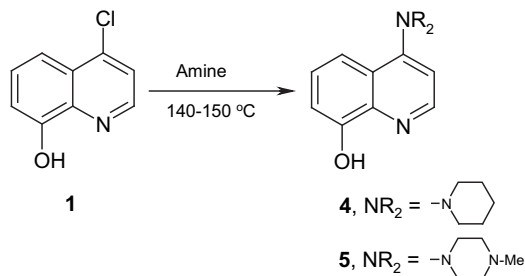
The new Al complexes are equipped with chloro, pyrazolyl, and 3-methylpyrazolyl groups as electron withdrawing substituents, and piperidinyl and *N*-methylpiperazinyl groups as electron donating substituents at C-4 of the 8-hydroxyquinolate ligand. The photoluminescence emission wavelengths of the new complexes have been measured and their relative photoluminescence quantum yields have been calculated.⁴²

DSC measurements together with powder X-ray analysis indicated clearly that two of the new Alq₃ derivatives (complexes **9** and **10**) are amorphous materials with high transition glass temperatures and no sharp melting endotherms.

To illustrate the high efficiency of the new Alq₃ derivatives as emitters in OLEDs, low cost devices have been fabricated with polyvinylcarbazole (PVK)^{43–45} as the hole transporting layer and with the complexes **7**, **9**, **10**, and commercially available Alq₃ as emitters. CsF/Al was used as the cathode due to its high efficiency.^{8,46}

2. Results and discussion

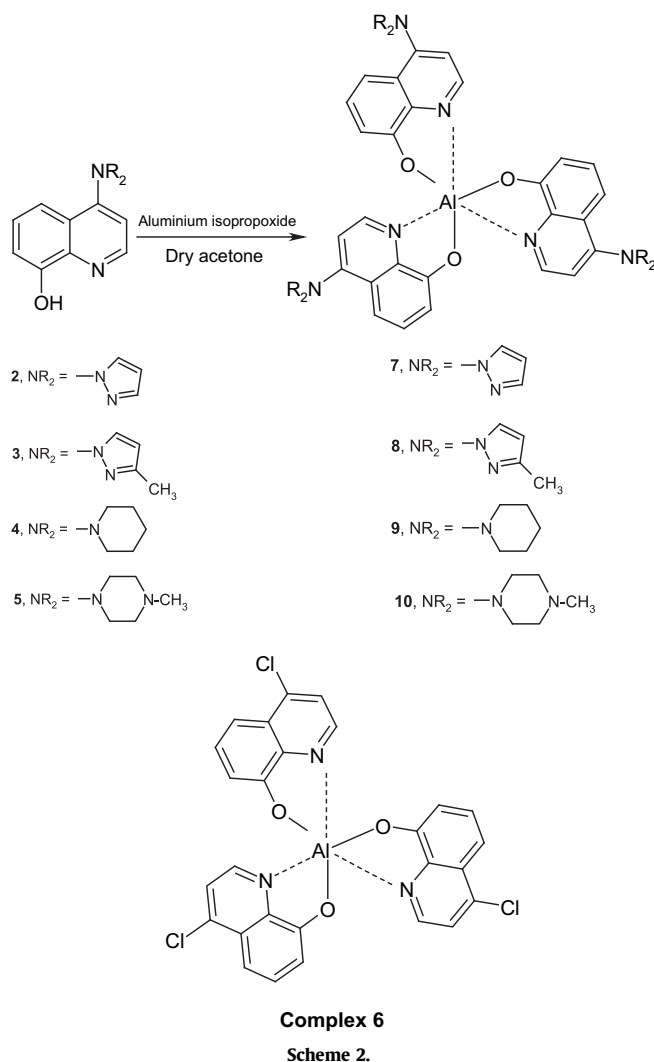
Five new aluminum complexes have been prepared from five ligands derived from 8-hydroxyquinoline. One of the complexes has a chloro substituent at C-4 and the other four complexes are equipped with nitrogen functionalities at position-4 of the quinolate ligand. The synthetic procedures for 4-chloro-quinolin-8-ol **1**, 4-pyrazol-1-yl-quinolin-8-ol **2**, 4-(3-methylpyrazol-1-yl)-quinolin-8-ol **3** have been described elsewhere.⁴⁷ The other two new ligands, 4-piperidin-1-yl-quinolin-8-ol **4** and 4-(4-methylpiperazin-1-yl)-quinolin-8-ol **5** were synthesized by the reaction between 4-chloro-8-hydroxyquinoline **1** and piperidine or *N*-methylpiperazine, respectively at 150–160 °C under solvent free conditions (Scheme 1). When the reaction was completed, water was added to the mixture to dissolve the amine hydrochloride formed. The resulting precipitate was filtered and dried under vacuum. The solvent free conditions offer a fast reaction (1–3 h), high and pure yields of ligands **4** and **5** (95% and 88%, respectively) and no protection for the hydroxyl group at C-8 of the 8-hydroxyquinoline was needed during the reaction. The new ligands were characterized by ¹H NMR and ¹³C NMR spectroscopy, HRMS and IR.



Scheme 1.

The aluminum complexes of all the previously mentioned ligands (ligands **1–5**) were prepared by heating the ligand (3 equiv) with aluminum isopropoxide (1 equiv) in dry acetone for 24 h at reflux under a nitrogen atmosphere (Scheme 2). Al Tris(4-

chloroquinolin-8-ol) **6**, Al tris(4-pyrazol-1-yl-quinolin-8-ol) **7**, Al tris(4-(3-methylpyrazol-1-yl-quinolin-8-ol)) **8** were gradually precipitated from the reaction mixture. The precipitated complexes were filtered and washed with cold acetone. Al Tris(4-piperidin-1-yl-quinolin-8-ol) **9** and Al tris{4-(4-methylpiperazin-1-yl-quinolin-8-ol)} **10** didn't precipitate during the reaction and therefore, the reaction mixtures were concentrated and treated with petroleum ether. The precipitates formed were collected by filtration and the complexes were dried under vacuum. The high solubility of complexes **9** and **10** can be attributed to the saturated piperidine and *N*-methylpiperazine substituents at C-4. The new Alq₃ derivatives were characterized by ¹H NMR and ¹³C NMR spectroscopy, IR and HRMS. The ¹H NMR spectra at room temperature of the new complexes showed the presence of meridional isomers only.⁴⁸



Complex 6
Scheme 2.

2.1. DSC measurements

The DSC thermograms of complexes **6–8** show sharp melting endotherms (378, 403, and 353 °C, respectively) and they are very similar to the DSC thermogram of the parent Alq₃. The blue shifted Alq₃ derivatives **9** and **10** show completely different DSC behaviour than the complexes **6–8** and the parent Alq₃ because up to 550 °C no melting endotherms could be observed. However, clear glass transition endotherms could be observed at 196 °C (complex **9**) and at 216 °C (complex **10**). The absence of melting endotherms

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