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Synthesis, characterization and DFT investigation of aluminum complexes of aryl- substituted-8-hydroxyquinoline

FakhrEldin O. Suliman*, Saleh N. Al-Busafi, Moza Al-Risi, Khalifa N. Al-Badi

Department of Chemistry, College of Science, Sultan Qaboos University, Box 36, Al-Khod 123, Sultanate of Oman, Oman

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1. Introduction

The unique fluorescence signature of 8-hydroxyquinoline has been used as the platform for the qualitative and quantitative analysis of several metal cations in solution. 8-hydroxyguinoline (8-HQ) exhibits feeble fluorescence emission in aqueous media and in many organic solvents. This weak fluorescence emission from 8-HQ has been attributed to the photoinduced tautomerization followed by nonradiative relaxations involving excited state proton transfer (ESPT) [1]. The intramolecular hydrogen bonding between the hydroxyl and the pyridyl groups is stronger in the excited state which results in deactivation of this state via internal conversion [2]. In chemical analysis, the bidentate 8-HQ is used to complex metal ions such as Al(III) and Zn(II), and the resultant 8hydroxyquinolinato-metal complex exhibits an intense fluorescence signal. This allows the development of straightforward sensitive protocols for the analysis of these metal ions where the intensity of the emitted light is directly proportional to the amount of the metal ion.

The most widely used methods for the analysis of aluminum are based on the sensitive atomic absorption and atomic emission techniques, such as graphite atomic absorption and inductively

ABSTRACT

New aryl substituted 8-hydroxyquinoline derivatives have been synthesized. The compounds were characterized by ¹H, ¹³C-NMR spectroscopy and mass spectrometry. The aluminum complexes of these derivatives show strong green emission in the range 530–535 nm with high quantum yield compared to the parent tris (8-hydroxyquinolinato)aluminum(III) complex. The structure of the aryl-substituted 8-hydroxyquinoline aluminum complexes in the ground state have been optimized at the B3LYP/6-31G* level of theory. The parent 8-hydroxyquinoline has also been examined using this method with the same basis set. A clear correlation between the shortening of the Al-N bond and red shift in the fluorescence emission band was observed. We have also found that substitution at the 5 and 7 position of the 8-hydroxyquinoline ligand cause simultaneous energy lowering of both highest occupied molecular orbital and the lowest unoccupied molecular orbital with the 5, 7-aryl substituted derivatives exhibiting the greatest effect.

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coupled plasma (ICP) with optical and mass detection systems. These methods, although sensitive, require expensive instrumentation, and considerable expertise for the analysis of aluminum. On the other hand molecular luminescence techniques offer alternative methods with many advantages for the analysis of metal ions. These techniques are sensitive, selective, cost effective and user friendly and require less maintenance compared to ICP techniques.

The requirements for highly sensitive fluorescence methods hinge in many cases on the characteristics of the complexing dye. Therefore, development of new dyes which emit at longer wavelengths and with high quantum yields when complexed with metal ions is desirable. Tuning of the tris (8-hydroxyquinolinato)aluminum(III) (Alq₃) fluorescence is an active area of research [3–14]. A number of experimental and theoretical approaches have been attempted to describe the geometrical characteristics of the quinolinolate ligand. Density functional theory (DFT) calculations performed on the meridional (*mer*) Alq₃ indicated that the highest occupied molecular orbital (HOMO) are located predominantly on the phenoxide side of the ligand, especially at the C5 position and C7 position of the quinolinolate ligand. The lowest unoccupied molecular orbital (LUMO), on the other hand, is mainly localized on the residual pyridyl side of the quinolinolate ligand [13–15].

Tris (8-hydroxyquinolinato)aluminum(III) (Alq₃) is currently entering the center of research interest especially after becoming a key component for the development of organic light-emitting





^{*} Corresponding author. Tel.: +968 24141480; fax: +968 24141469. *E-mail address:* fsuliman@squ.edu.om (F.O. Suliman).

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diodes (OLEDs), an important material currently used as electron injection, electron transport and emitting layer in flat panel display systems [16]. Enhancement of the photoluminescence and electroluminescence quantum yields of 8-HQ based OLEDs has been attempted via modification of the quinolinolate ligand. Several derivatives of 8-HQ were synthesized and used to prepare aluminum complexes as light emitting diodes. The most attractive strategy used depends on the introduction of electron withdrawing and electron donating groups into the 8-HQ ligands [4–6,8–10,17,18]. Substitution of methyl groups at C2 and C4 of the quinolinolate ligand results in aluminum complexes that presented high photoluminescence and electroluminescence efficiencies [9,10]. Also tuning of the emission of the aluminum quinolinolate system has been achieved with introduction of electron withdrawing and electron donating phenyl moieties at the C5 position of the 8-HQ ligand. The nature of phenyl substituents was found to profoundly affect the emission color as well as the quantum yield of the resultant complexes [3,5,6,17].

In the present work, we report the synthesis of two new phenyl substituted Alq₃ dyes derivatized at the 5 and 7 positions of the 8-HQ ligand. The spectroscopic properties of the complexes were investigated and compared to those of the phenyl substituted derivatives at C5 and the parent Alq₃. Furthermore, DFT-B3LYP methods were used to optimize and study the ground state of these complexes.

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich and used without purifications. All solvents were used as received or were purified using standard procedures [19]. Spectroscopic grade solvents (Aldrich) were used for the fluorescence and UV–Visible measurements.

2.2. Methods and instruments

Infrared spectra were recorded on a Perkin–Elmer FT-IR BX system in KBr pellets. Maximum absorptions were recorded in wave numbers (cm⁻¹). Melting points were measured by Gallen–Kamp apparatus. ¹H and ¹³C NMR spectra were performed on a 400 MHz Bruker spectrometer using tetramethylsilane (TMS) as the internal standard and CDCl₃ or DMSO-*d*₆ as the solvent at room temperature. UV–Vis spectra were performed on Varian CARY 50 spectrophotometer. Fluorescence spectra were recorded on a Perkin Elmer LS55 Luminescence spectrophotometer. Mass spectra were measured using Quatro ultima pt (Waters Corp. MA, USA) instrument.

2.3. Synthesis

5-(*p*-Cyanophenyl)-8-hydroxyquinoline (**4a**) and 5-(*p*-acetyl-phenyl)-8-hydroxyquinoline (**4c**) were synthesized by the recently reported method [3,6].

2.3.1. 8-Benzyloxy-5,7-dibromoquinoline(2b)

A mixture of 5,7-dibromo-8-hydroxyquinoline (**1b**) (3.0 g, 9.9 mmol), benzyl chloride (1.38 g, 10.9 mmol), potassium carbonate (1.37 g) and potassium iodide (0.162 g, 0.98 mmol) in acetone (60 mL) was refluxed under N₂ for 10 h. The mixture was poured into water, filtered, and washed with water. The crude product was recrystallized from ethanol and dried *in vacuo*. Yield: 56.8%. M.p.: 117.8 °C–119.2 °C. IR(cm⁻¹): v = 3090 (C–H)_{arom}, 2962 (C–H), 1574 (C=C)_{arom}, 1490 (C–N). ¹H NMR (400 MHz, CDCl₃):

δ(ppm) = 8.79 (dd, 1H, J = 1.6 Hz and 4.2 Hz, H2), 8.46 (dd, 1H, J = 1.6 Hz and 8.6 Hz, H4), 7.97 (s, 1H, H6), 7.52 (dd, 1H, J = 4.2 Hz and 8.6 Hz, H3), 7.36–7.6 (5H, arom-H), (5.46 (s, 2H, CH₂). ¹³C NMR (100.4 MHz, CDCl₃): δ (ppm) = 151.1, 122.3, 136.4, 128.8, 122.9, 134.0, 117.2, 152.7, 137.4,116.7, 144.3, 128.5, 129.1, 128.6. EI-MS (m/z): calculated for [C₁₆H₁₁Br₂NO], 393.10; found, 393.12.

2.3.2. 8-Benzyloxy-5,7-bis(p-cyanophenyl)quinoline (3b)

A mixture of 8-benzyloxy-5,7-dibromoquinoline (2b) (1.0 g, 2.5 mmol), 4-cyanophenylboronic acid (0.82 g, 5.6 mmol), sodium carbonate (1.07 g, 10 mmol), toluene (9.96 mL), ethanol (4.98 mL), and water (7.47 mL) was degassed under N2 for 30 min. To the mixture was added Pd(PPh₃)₄ (0.18 g, 15 mmol) and the reaction was refluxed under nitrogen for 24 h. The crude product was extracted with toluene, recrystallized from ethanol, and dried in (Yield = 51.35%). M.P. = $207.5 \circ C - 209.5 \circ C$. IR(cm⁻¹): vacuo v = 3042 (C-H)_{arom}, 2227.55 (CN), 1601 (C=C) arom. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 9.08 (dd, 1H, J = 1.5 Hz and 4.1 Hz, H2), 8.17 (dd, 1H, J = 1.5 Hz and 8.6 Hz, H4), 7.49 (dd, 1H, J = 4.1 Hz and 8.6 Hz, H3), 7.44 (s, 1H, H6), 7.8 (d, 2H, J = 8.2 Hz, aromatic-H), 7.61 (d, 2H, J = 8.2 Hz, arom-H), 7.18 (d, 2H, J = 7.0 Hz, arom-H), 7.08 (d, 2H, J = 7.0 Hz, arom-H), 5.32 (s, 2H, -CH₂), 7.22 (m, 3H, arom-H), 7.67 (m, 2H, arom-H). ¹³C NMR (100.4 MHz, CDCl₃): δ (ppm) = 150.7, 121.1, 134.7, 129.1, 132.7, 129.2, 127.5, 152.5, 144.0, 112.2, 137.0, 131.1, 132.8, 132.7, 134.3, 133.9, 128.5, 127.89, 132.2, 131.2, 143.8, 142.9, 119.3, 119.0. EI-MS) *m*/*z*): calculated for [C₃₀H₁₉N₃O], 437.49; found, 437.41.

2.3.3. 8-Benzyloxy-5,7-bis(p-acetylphenyl)quinoline (3d)

A mixture of 5,7-dibromo-8-benzyloxyquinoline (2b) (2g, 5.1 mmol), 4-acetyl-phenylboronic acid (1.8 g, 11.2 mmol), sodium carbonate (2.2 g, 20 mmol), toluene (19.96 mL), ethanol (9.9 mL), and water (14.9 mL) was degassed under N₂ for 30 min. To the mixture was added Pd(PPh₃)₄ (0.35 g, 0.30 mmol) and the reaction was refluxed under nitrogen for 24 h. The crude product was extracted with toluene, recrystallized from ethanol, and dried in *vacuo*. Yield = (52.1%). M.p.: 163–164 °C. IR (cm⁻¹): v = 3100(C-H)_{arom}, 2962 (C-H), 1682 (C=O). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 9.05 (dd, 1H, J = 1.6 Hz and 3.9 Hz, H2), 8.22 (dd, 1H, *J* = 1.6 Hz and 8.6 Hz, H4), 8.10 (d, 2H, *J* = 5.1 Hz, arom-H), 7.99 (d, 2H, *J* = 6.7 Hz, arom-H), 7.73(d, 2H, *J* = 5.1 Hz, arom-H), 7.61 (d, 2H, J = 6.7 Hz, arom-H), 7.52 (s, 1H, H6), 7.44 (dd, 1H, J = 3.9 Hz and 8.6 Hz, H3), 7.17 (m, 5H, arom-H), 5.27 (s, 2H, CH₂), 2.68 (s, 3H, CH₃), 2.65 (s, 3H, CH₃). ¹³C NMR (100.4 MHz, CDCl₃): δ (ppm) = 150.44, 128.56, 135.35, 128.93, 130.75, 128.73, 128.47, 152.26, 144.26, 128.23, 137.42, 130.58, 131.52, 130.68, 129.48, 129.02, 198.28, 198.05, 134.56, 133.28, 143.90, 143.25, 136.75, 136.31, 127.86, 127.49. EI-MS) m/z): calculated for [C₃₃H₂₉NO₃], 471.55; found, 471.70.

2.3.4. 5, 7-Bis(p-cyanophenyl)-8-hydroxyquinoline (4b)

A mixture of 8-benzyloxy-5,7-bis(*p*-cyanophenyl)quinoline (**3b**) (0.57 g, 1.3 mmol), Pd/C (10 wt%, 0.40 g), and cyclohexa-1,4-diene (2.0 g) in absolute ethanol (15.0 mL) was refluxed under N₂ for 5 h. The mixture was filtered, and ethanol was evaporated. The product was recrystallized from ethanol/water and dried *in vacuum*. (Yield = 61%). M.p. = 264–265 °C, IR (cm⁻¹): v = 3042 (C–H)_{arom}, 1359 (CN), 1602 (C=C)_{arom}. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.85 (dd, 1H, J = 4.2 Hz and 1.5 Hz, H2), 8.21 (dd, 1H, J = 8.5 Hz and 1.5 Hz, H4), 7.96 (d, 2H, J = 8.2 Hz, arom-H), 7.81 (d, 2H, J = 8.1 Hz, arom-H), 7.78 (d, 2H, J = 8.2 Hz, arom-H), 7.61 (d, 2H, J = 8.1 Hz, arom-H), 7.52(dd, 1H, J = 4.2 Hz and 8.5 Hz, H3), 7.26 (s, 1H, H6). ¹³C NMR (100.4 MHz, CDCl₃): δ (ppm) = 148.6, 122.8, 134.0, 129.1, 130.7, 126.0, 120.2, 149.79, 138.69, 132.5, 132.2, 111.6, 111.0, 129.9, 129.3, 143.7, 141.8, 118.9, 118.6. EI-MS) *m*/*z*): calculated for [C₂₃H₁₃N₃O], 347.11; found, 347.18.





Fig. 1. The geometry of mer-Alq3, labels a-c a for the quinolinate ligands.

2.3.5. 5, 7-Bis(p-acetylphenyl)-8-hydroxyquinoline (4d)

A mixture of 8-benzyloxy-5, 7-bis(p-acetylphenyl)quinoline (3d) (0.62 g, 1.3 mmol), Pd/C (10 wt%, 0.40 g), and cyclohexa-1,4diene (0.93 g) in absolute ethanol (12.0 mL) was refluxed under N₂ for 5 h. The mixture was filtered, and ethanol was evaborated. The product was recrystallized from ethanol/water and dried in *vacuum.* (Yield = 65%). M.p. = 172.9–174.8 °C. IR(cm⁻¹): v = 3064(C-H)_{arom}, 2929 (C-H), 1680 (C=O), 1603 (C=C). ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3)$: δ (ppm) = 8.86 (dd, 1H, J = 1.1 Hz and 4.1 Hz, H2), 8.26 (dd, 1H, J = 1.1 Hz and 8.5 Hz, H4), 8.10 (d, 2H, J = 8.4 Hz, arom-H), 8.08 (d, 2H, *J* = 8.4 Hz, arom-H), 7.94 (d, 2H, *J* = 8.4 Hz, arom-H), 7.64 (s, 1H, H6), 7.61 (d, 2H, J = 8.4 Hz, arom-H), 7.48 (dd, 1H, J = 4.1 Hz and 8.5 Hz, H3), 2.87 (s, 3H, CH₃), 2.68 (s, 3H, CH₃). ¹³C NMR (100.4 MHz, CDCl₃): δ (ppm) = 149.7, 122.9, 136.2, 129.1, 130.7, 128.9, 126.4, 197.0, 142.5, 130.1, 129.8, 198.1, 198.0, 134.7, 132.9, 148.7, 144.3, 139.0, 136.6, 122.8, 121.4. EI-MS) *m*/*z*): calculated for [C₂₆H₂₃NO₃], 381.42; found, 381.48.

2.4. Computational details

The general structure of the investigated complexes is shown in Fig. 1. The labels a-c are used to distinguish the three quinoline ligands complexed to the central aluminum atom. The results of the theoretical calculations are reported according to the labeling shown here in Fig. 1. The ground state geometries of Alq₃ and its phenyl substituted derivatives were fully optimized using Becke's three parameter hybrid functional combined with Lee, Yang and Parr (LYP) correlation [20,21] denoted as B3LYP with the 6-31G* basis set. All computations were performed using *Gamess-US* package [22].

3. Results and discussion

3.1. Synthesis

The synthesis of the aryl substituted ligands **4a**–**4b** starts from 5-bromo-8-hydroxyquinoline and 5, 7-dibromo-8-hydroxyquinoline (**1a**, **1b**), respectively. The Benzyl derivative of **1a** (**2a**) and **1b** (**2b**; Scheme 1) were first synthesized from the bromo-substituted 8-hydroxyquinolines **1a** and **1b** and then underwent a Suzuki coupling reaction with 4-cyanophenylboronic acid or 4-acetyl-phenylboronic acid to give **3a**–**3d**. Debenzylation gave **4a**–**4d**. The structures of the ligands were confirmed by ¹H, ¹³C-NMR, and IR spectroscopy and mass spectrometry. The aluminum complexes of 8-HQ, and derivatives **4a**–**4d** were prepared in methanol.

3.2. Formation of (qunolinolato) aluminum (III) and their spectral properties

We used UV–Visible and fluorescence spectroscopy to investigate the formation of the aluminum (III) quinolinates of the aryl substituted derivatives of 8-hydroxyquinoline. The absorption spectra of all derivatives are characterized by a very intense π – π * absorption bands at around 250 nm accompanied by a less intense and broader band above 300 nm. In all cases, the absorption bands shift to longer wavelengths by 5–13 nm when cyanophenyl and acetylphenyl groups are attached to C5 and C7 of the 8-hydroxyquinoline ligand. Upon coordination of these ligands with aluminum in methanol the π – π * absorption maxima exhibited a red shift compared to the ligands as well as a noticeable increase in the quantum yield due to the extension of conjugation of the quinoline chromophores. Also the aryl-substituted complexes exhibited a red shift compared to the parent Alq₃ complex.



Scheme 1. Syntheses of aryl-substituted 8-hydroxyquinoline.

Fig. 2 shows the fluorescence emission of Alq_3 and for the complexes of **4a–4d** with aluminum in methanol. Typically the emission bands for the aryl substituted aluminumguinolinates shift to longer wavelength by 8-13 nm. The 5, 7-aryl substituted aluminumquinolinates exhibited shifts to longer wavelengths compared to the 5-aryl-substituted derivatives. The fluorescence emission is greatly enhanced when an electron poor group is attached to C5 and C7 of the quinoline ligand. It is clear from Fig. 2 that the cyanophenyl substituted derivatives exhibited a slightly more intense fluorescence compared to the acetylphenyl substituted derivative. Moreover, the 5, 7-aryl substituted derivatives show a much higher enhancement in the fluorescence emission. The addition of aryl rings to 8-hydroxyquinoline results in the extension of the conjugation which results in an increase in the fluorescence intensity of the chelates of these ligands with aluminum (III).

The rate of fluorescence photon emission, $\Phi_{\rm F}$ is related to the fluorescence quantum yield, $\varphi_{\rm F}$ by the following equation [23]

$$\Phi_{\rm F} = n_{\rm S_0} k_{\rm A} \varphi_{\rm F} V \tag{1}$$

where n_{S_0} is the number density of the ground state (in molecules per cm³), k_A is the rate of absorption, V is the sample volume and φ_F is the quantum efficiency.

The rate constant of fluorescence, $k_{\rm F}$ and $\varphi_{\rm F}$ are expected to be large if the transition probability between S₀ and S₁ is large. It is known that absorption to S₁ and fluorescence involve the same electronic states, therefore both $k_{\rm F}$ and $k_{\rm A}$ (S₀ \rightarrow S₁) are larger for molecular systems that possess large molar absorptivity (ε). On the other hand, the most efficient fluorescence usually associates with $\pi\pi^*$ transitions and these are characterized by large ε , $k_{\rm A}$ and $k_{\rm F}$. Therefore, there is always an increase in $\varphi_{\rm F}$ with the extension of the conjugation system.

Fig. 3 shows the titration curves for the 5-acetylphenyl and 5, 7acetylphenyl substituted derivatives with AI^{3+} in methanol using an excitation wavelength of 290 nm. This figure shows a clear growing green band at 530 nm accompanied by a band at shorter wavelength (390 nm) with the presence of clear isoemissive points. The presence of an isoemissive point indicates that at least two excited species are involved in the emission spectra. In fact, the



Fig. 2. Fluorescence spectra (λ_{ex} 390) of (1) Alq₃ (2) Al-4c (3) Al-4a (4) Al-4d (5) Al-4b in methanol.



Fig. 3. Titration curve of 2×10^{-6} M of (a) **4c** and (b) **4d** with Al³⁺ showing a growing green emission in methanol. [Al³⁺] = 0, 0.1 μ M, 0.2 μ M, 0.4 μ M, 0.6 μ M, 0.8 μ M, 1.0 μ M, 2.0 μ M and 3.0 μ M, from bottom to top.

observation of an isoemissive point is a clear indication that two emitting species are present in equilibrium in the reaction mixture, possibly the free ligand and its aluminum complex. The stoichiometry of the metal: ligand studied by the molar ratio and the continuous variation methods was found to be 1: 3 for all derivatives. Similar results were obtained for the *p*-cyanophenyl substituted ligands. These ligands can, therefore, be used as excellent candidates for sensing aluminum ions in various media.

3.3. Molecular geometries

To further scrutinize the structure of the synthesized complexes the ground state geometry of Alq₃ and its aryl substituted derivatives were optimized using B3LYP methods. In Table 1, we present some selected parameters of the optimized geometries of Alq₃ and

 Table 1

 Selected B3LYP/6-31G* optimized geometries of the ground electronic state.

R (Å), φ (deg)	Al-8HQ	Al- 4a	Al- 4b	Al- 4c	Al- 4d	Experimental ^a
Al-N ₁	2.084	2.080	2.071	2.086	2.076	2.050
Al-N ₂	2.126	2.122	2.089	2.121	2.066	2.087
Al-N ₃	2.064	2.066	2.054	2.063	2.144	2.017
Al-O ₁	1.855	1.858	1.894	1.865	1.890	1.850
Al-O ₂	1.881	1.881	1.913	1.893	1.883	1.860
Al-O ₃	1.884	1.879	1.916	1.893	1.891	1.857
N ₁ -Al-N ₃	171.6	170.9	169.0	170.4	171.4	
N ₂ -Al-O ₁	172.5	172.4	171.7	172.1	172.4	
$O_2 - Al - O_3$	166.6	166.8	166.8	165.9	166.7	
Φ_1^{o}	-	49	52	50	53	
Φ_2^{o}	-	-	33	_	38	

^a Alq₃ X-ray data from reference [22]. Φ_1^0 dihedral angle between 5- substituted phenyl group and the quinoline nucleus. Φ_2^0 dihedral angle between 7-substituted phenyl group and the quinoline nucleus.

its aryl substituted derivatives. For comparison we also included the X-ray experimental results of the parent Alq₃ complex in Table 1 [24]. We clearly observe from this table the good agreement of experimental and calculated data for Alq₃. This indicates the reliability of the computational method adopted in this study for the delineation of the structure of the aryl substituted derivatives of aluminum quinolinate.

As shown in Table 1, the bond lengths of Al—N and Al—O are only slightly affected upon substitution of an aryl moiety at the C5 and C7 positions of the quinoline ligand. The spectral shift of absorption

and emission wavelength depends on a fine balance of electronic transition between the quinolinolate dyes and the aryl substituents at C5 and C7. It has been reported that some C5 substituted guinolinolate ligands exhibit a significant degree of non-coplanarity with dihedral angles $> 50^{\circ}$ between the planes of the quinoline and the arvl substituents as shown by X-ray crystallography [3]. This results in the reduction of the degree of conjugation between the two moieties and consequently the efficacy of electronic interactions. Inspection of the DFT optimized structures reveals that the dihedral angles between the planes of the aryl substituent and the quinoline groups at C5 are between $49^{\circ}-53^{\circ}$ (Table 1). These results correlate well with those obtained by X-ray crystallography [3]. On the other hand the dihedral angles between the C7 substituent and the quinoline group is 33° and 38° for the p-cyanophenyl and *p*-acetylphenyl derivatives respectively. Clearly, from these results one can conclude that the presence of another aryl substituent at C7 increases the efficiency of electronic communication with the quinoline group.

We also calculated the frontier molecular orbitals (FMOs) for Alq_3 and its aryl substituted derivatives using the optimized ground state geometries. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for Alq_3 and its aryl substituted derivatives are shown in Fig. 4. The HOMO in all complexes shows almost the same trend and is localized at ligand *a*. On the other hand, the LUMO is predominantly localized at ligand *b*. These results are in agreement with the previously reported



Fig. 4. The molecular orbital surfaces of the (a) HOMO (b) LUMO of mer-Alq₃ and its aryl-substituted derivatives.



complexes [7,12,14,25]. In Table 2 we list the calculated energies of the HOMO and LUMO of the studied complexes. It is observed from these results that the presence of an aryl moiety at C5 stabilizes simultaneously the HOMO and the LUMO eigenvalues. Further stabilization of the HOMO and the LUMO is observed when substitution of another aryl moiety occurs at C7. Interestingly, the HOMO and LUMO energy gap (E_g) of the investigated complexes show a decrease with substitution that correlates well with the red shift observed for emission bands. The calculated energy gaps for the 5-aryl substituted derivatives also agree well with the experimental values [3] as shown in Table 2. Also it is clear from Table 2 that the absorbance wavelengths of the complexes correlate well with the energy gap and a clear red shift is observed for all complexes. The maximum shift was obtained for Al-4b which is in line with results obtained by the theoretical model. It is worth mentioning here that more accurate simulation of the electronic spectra requires further computations using time-dependent density functional theory (TD-DFT) [26].

Table 2

The HOMO, LUMO and gap energies calculated by the DFT-B3LYP/6-31G * method.

Compound	$\lambda_{abs} (nm)$	E _{HOMO} (au)	E _{LUMO} (au)	E _g (au)
Alq ₃	380	-0.1806	-0.0602	0.1204
Al- 4a	393	-0.1992	-0.0831	0.1161 (0.1128) ^a
Al- 4b	405	-0.2148	-0.1052	0.1096
Al- 4c	389	-0.1905	-0.0777	0.1128 (0.1091) ^a
Al- 4d	397	-0.1964	-0.0831	0.1133

^a From reference [3].

It has been reported that the energy of the LUMO greatly influence the turn-on voltage in organic light emitting diodes (OLED) [12]. The injection energy of electrons from the cathode Al to the Alq₃ surface is calculated to be 2.4 eV [12]. This is indicative of the presence of a large energy barrier for the charge injection for Alq₃ which entails the use of a high turn-on voltage. Therefore, the occurrence of a lower LUMO will enhance the ability of electron injection. It is clear from this study that the simultaneous substitution at C5 and C7 of the quinolinate ligand could be an effective way to lower the LUMO levels in the alumiumquinolinate compounds. The *p*-cyanophenyl substituents lowered the LUMO by 0.79 eV and 1.16 eV for the 5-aryl substituted and 5, 7-aryl substituted ligands respectively. The acetylphenyl substituted ligands, however, lowered the LUMO level by 0.48 eV and 0.66 eV for the 5-aryl substituted and the 5, 7-aryl substituted derivatives, respectively.

4. Conclusion

We have prepared two new aryl substituted 8-hydroxyquinoline derivatives and their metal complex dyes with Al(III). Furthermore, their spectroscopic properties were compared with those of the 5-aryl substituted derivatives and the parent Alq₃ complex. It has been shown that these new dyes exhibit a higher quantum yield as compared to Alq₃. These compounds emit in the range of 530–535 nm. The ground state of these metal complex dyes have been optimized using the B3LYP/6-31G* level of theory. The calculations indicated some structural changes due to attachment

of electron poor substituents at C5 and C7 of the quinoline ligand. The Al–N bond lengths were correlated to the experimental spectral shifts. Stabilization of the HOMO and the LUMO eigenvalues is also observed and the energy gap E_g correlates well with the observed spectral changes.

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