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# Synthesis, characterization and DFT calculation of 4-fluorophenyl substituted tris(8-hydroxyquinoline)aluminum(III) complexes



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### HIGHLIGHTS

### G R A P H I C A L A B S T R A C T

- Synthesis and characterization of new 4-fluorophenyl derivatives of 8hydroxyquinoline.
- Emission spectra of the aluminum complexes of the new ligands show red shift.
- Theoretical calculations were performed using TD-DFT methods coupled to B3LYP/6-31G(d) level of theory.
- Electronic structure and properties were presented.
- HOMO-LUMO energies and contributions from different groups were obtained.

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### ABSTRACT

New 4-fluorophenyl substituted 8-hydroxyquinoline derivatives, 5-(4-fluorophenyl)quinolin-8-ol and 5,7-bis(4-fluorophenyl)quinolin-8-ol, were synthesized and characterized by spectroscopic methods. The aluminum complexes of 5-(4-fluorophenyl)quinolin-8-ol (AlQF) and of 5,7-bis(4-fluorophenyl)quinolin-8-ol (AlQF2) exhibit strong fluorescence emission centered at 525 nm and 530 nm respectively. The quantum yield of both complexes were enhanced compared to the parent tris(8-hydroxyquinolinato)aluminum(III) complex. Electronic structures and photophysical properties of the new complexes were investigated theoretically by *ab initio* and density functional theory (DFT) and time dependent DFT (TD-DFT). Geometries of the ground state (S<sub>0</sub>) and the first excited state (S<sub>1</sub>) of the new complexes were optimized at the B3LYP/6-31G(d) functional and configuration interaction singles (CIS) method respectively. The aryl substituents were found to contribute significantly to the frontier molecular orbitals (FMOs). We have observed that in both cases the lowest occupied molecular orbital (LUMO) energy decreases while the energy of the highest occupied molecular orbital is slightly increased. The most significant increase was observed for AlQF2.

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### Introduction

8-Hydroxyquinoline (HQ), a well-known bidentate chelating ligand, has been historically employed in gravimetric analysis to selectively bind and precipitate metal ions by tuning of the pH of the media [1,2]. But by the end of the eighties of last century, these ligands has emerged as a center of extensive scientific and

technological interest following the introduction of small molecules light emitting diodes (OLEDs) by Tang and Van Slyke [3]. The high thermal stability, excellent electron transport properties and the unique emissive properties qualified tris(8-hydroxyquinoline)aluminum(III) (AlQ) to play a pivotal role in the development of OLEDs that lead to the introduction of flat panel display technology. This step has stimulated researchers to develop many aluminum complexes using new derivatives of 8-hydroxyquinoline [4–12] and equally to develop complexes of HQ and its derivatives with other metal ions such as gallium and indium has received a

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considerable interest [4,8,13–18]. Of special interest is the tuning of the emission color of OLEDs via introduction of various substituents in 2, 4, or 5 and 7 positions of the quinolate ligand.

A number of studies performed on mer-AlQ have revealed the location of the highest molecular orbital (HOMO) to be mainly on the phenoxide side whereas the lowest unoccupied molecular orbital (LUMO) density found in the pyridyl side [19-37]. This distribution, therefore, suggests that substitution on the phenoxide ring will predominantly affects HOMO, while substitution on the pyridyl ring will affect more LUMO. For instance locating electron donating groups in 2, 3 and 4 position of HQ ligands destabilizes LUMO and as a result its energy increases leading to larger HOMO-LUMO energy gap. On the other side, substitution of electron withdrawing groups in positions 5, 6 or 7 of the HQ ligand is expected to cause a blue shift of the maximum emission wavelengths due to an increase in the transition energy. By this notion many research groups has attempted the design and synthesis of new aluminum quinolate complexes with desirable characteristics such as high stability, tunable emission color and intensity by introducing various substituents at the phenoxide and pyridyl sides of HQ.

Investigation of efficient emitters possessing high fluorescence intensity, higher thermal stability, proper hole transport and charge injection properties has been the focus of an intense research during the past decade [5,7,8,11,12,16,18,38,39]. Modification of AlQ by altering the HOMO-LUMO energy gap and consequently tuning of the emission energy has been attempted via substitution of groups at various positions of the quninolinate ligand. For instance, substitution of a methyl group in the pyridyl ring resulted in enhancement of the luminescence quantum yield of the resultant Al<sup>3+</sup> and Ga<sup>3+</sup> complexes [4]. On the other hand, manipulation of the HOMO electronic density have been achieved by substitution of electron withdrawing groups at the phenoxide side of the quinolate group [6,7,10,11,31]. By this strategy the energy of the  $\pi$ - $\pi^*$  transition increases leading to a shift of the emission wavelength to the blue region. However, inspection of the literature reveals the fact that substitution of electron withdrawing groups at C5 failed to produce such shift. Tuning of the emission wavelength through substitution of arvl substituents at C5 have been reported to span most of the visible region specially the green to red part of the spectra [5,6,40]. An interesting scenario to produce blue emitting complexes based on AlQ platform has been reported recently by Anzenbacher et al. [7]. The blue shifted emission was achieved by combining substitutions of an electron donating group at C4 together with and electron withdrawing group at C6 of the quinoline ligand. Furthermore, using a time-dependent functional theory (TD-DFT) it has been demonstrated that substitution of CH-groups in the positions 2-7 of the quinolinate ligand by nitrogen atoms could impart significant tuning of the emission wavelength over the whole visible range (400-700 nm) [24]. In this case the 5-substituted derivative was predicted to produce the most effective blue shift whereas the most important red shift was obtained for the 4-substituted one.

In this paper we describe the synthesis and characterization of 4-fluorophenyl mono-substituted HQ ligands at position 5 and a disubstituted 4-fluorophenyl HQ at positions 5 and 7. Moreover we report on the photoluminescent properties and TD-DFT theoretical calculations of their aluminum complexes.

### Experimental

### Materials

All reagents were purchased from Aldrich and used without purification. All solvents were used as received. Spectroscopic grade solvents (Aldrich) were used for the fluorescence and UV–Visible measurements

### Apparatus

Melting points were measured by GallenKamp apparatus (UK). <sup>1</sup>H and <sup>13</sup>C NMR spectra were performed on a 400 MHz Bruker spectrometer (Bruker, Germany) using tetramethylsilane (TMS) as the internal standard and CDCl<sub>3</sub> as the solvent at room temperature. UV–Visible spectra were recorded on Varian CARY 50 spectrophotometer (VARIAN, Australia). Fluorescence spectra were recorded on a PerkinElmer LS55 Luminescence spectrophotometer (PerkinElmer, UK). pH of the buffer solutions were measured using WTW pH meter pH320 (Germany).

### Synthesis

Mono substituted 4-fluorophenyl HQ (5-(4-fluorophenyl)quinolin-8-ol) was synthesized using literature methods [5]. While the synthesis of a di substituted 8-hydroxyquinoline (5,7-(4-fluorophenyl)-8-hydroxyquinoline) is performed similar to our previous work [12] and is outlined below.

### 5,7-Dibromo-8-benzyloxyquinoline (2a)

5,7-Dibromo-8-hydroxyquinoline **(1a)** (2.535 g, 8.37 mmol) was mixed with benzyl chloride (1.15 g, 9.09 mmol), potassium carbonate (1.14 g) and potassium iodide (0.135 g) in 50 mL acetone. The mixture was refluxed under nitrogen gas for 10 h. After reflux, the mixture was poured in water and the resulted solid was filtered and washed with water and re-crystallized from ethanol and dried in vacuum. The product was a light yellow solid and its melting point range is 119–120 °C. The product structure was confirmed by using NMR.  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 5.53 (2H, s), 7.31 (2H, dd,  $J_1$  = 6.8 Hz,  $J_2$  = 14.3 Hz), 7.51 (2H, dd,  $J_2$  = 4.4 Hz,  $J_2$  = 8.6 Hz), 7.61 (2H,d, J = 7.1 Hz) 7.96 (1H, s), 8.45 (1H, dd,  $J_1$  = 1.3 Hz,  $J_2$  = 8.5 Hz), 8.96 (1H, dd,  $J_1$  = 1.2 Hz,  $J_2$  = 4.0 Hz).

### 5,7-Di(4-fluorophenyl)-8-benzyloxyquinoline (3a)

5.7-Dibromo-8-benzyloxyquinoline (2a) (2.50 g. 6.45 mmol) was mixed with 4-fluorophenyl boronic acid (2.08 g, 14.86 mmol), toluene (25.25 mL), ethanol (12.63 mL), water (18.90 mL), sodium carbonate (2.71 g) and Pd(PPh<sub>3</sub>)<sub>3</sub> (0.449 g). The mixture was refluxed under nitrogen gas for 24 h. Then the product was extracted with toluene and re-crystallized from ethanol and dried in vacuum. The final product was a brownish yellow solid with mass of 1.987 g, (73.9%) yield and melting point range (106.2-106.5 °C). NMR;  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 5.13 (1H, s), 6.95 (4H, td,  $J_1$  = 2 Hz,  $J_2 = 6.8$  Hz,  $J_3 = 15.5$  Hz), 7.03 (3H, dd,  $J_1 = 2.3$  Hz,  $J_2 = 9.2$  Hz), 7.11 (4H, dd,  $J_1 = 4.2$  Hz,  $J_2 = 7.4$  Hz), 7.28 (1H, dd,  $J_1 = 4.1$  Hz,  $J_2 = 8.5$  Hz), 7.35 (1H, s), 7.48 (2H, td,  $J_1 = 2.1$  Hz,  $J_2 = 5.5$  Hz,  $J_3 = 12.1 \text{ Hz}$ ), 8.07 (1H, dd,  $J_1 = 1.6 \text{ Hz}$ ,  $J_2 = 8.5 \text{ Hz}$ ), 8.91 (1H, dd,  $J_1$  = 1.6 Hz,  $J_2$  = 4.0 Hz);  $\delta_C$  (100.4 MHz, CDCl<sub>3</sub>): 78 (C1), 115 (C2), 122 (C3), 126 (C4), 128 (C5), 129 (C6), 131 (C7), 132 (C8), 134 (C9), 135 (C10), 136 (C11), 138 (C12), 139 (C13), 145 (C14), 150 (C15), 153 (C16), 162 (C17), 164 (C18).

### 5,7-Di(4-fluorophenyl)-8-hydroxyquinoline (4a)

5,7-Di(4-fluorophenyl)-8-benzyloxyquinoline **(3a)** (1.52 g, 3.6 mmol) was mixed with Pd/C (1.07 g) and cyclohexa-1,4-diene (2.49 g, 31.08 mmol) in 34.0 mL ethanol. The mixture was refluxed under nitrogen gas for 10 h. The product was filtered and re-crystallized from ethanol/water and dried in vacuum. The final product was white product and its mass was 0.338 g and with percent yield of 28.4%. The melting point range of (117.8–118.3 °C).  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>): 7.13 (4H, td,  $J_1 = 2.1$  Hz,  $J_2 = 8.6$  Hz,  $J_3 = 16$  Hz), 7.38 (2H, dd,  $J_1 = 1.5$  Hz,  $J_2 = 4.3$  Hz), 7.42 (1H, dd,  $J_1 = 2$  Hz,  $J_2 = 5.5$  Hz), 7.52 (1H, s), 7.77 (2H, td,  $J_1 = 2.1$  Hz,  $J_2 = 5.5$  Hz,  $J_3 = 8.8$  Hz), 8.18 (1H, dd,  $J_1 = 1.4$  Hz,  $J_2 = 8.5$  Hz), 8.87 (1H, dd,  $J_1 = 1.4$  Hz,  $J_2 = 4.2$  Hz).  $\delta_{\rm C}$  (100.4 MHz, CDCl<sub>3</sub>): 78 (C1), 117 (C2),

122 (C3), 127 (C4), 130 (C5), 131 (C6), 132 (C7), 134 (C8), 136 (C9), 138 (C10), 140 (C11), 148 (C12), 162 (C13), 165 (C14).

# Preparation of aluminum complexes and measurement of photophysical properties

A mixture of the new ligands (0.15 mmol) and aluminum chloride hexahydrate (12 mg, 0.05 mmol) in degassed ethanol ( $\sim$ 5 mL) was refluxed for 3 h. The mixture was cooled to room temperature and neutralized by triethylamine ( $\sim$ 20 µL). 10 mL of water was added to the mixture and the precipitated complex was filtered off. The filtered precipitate was washed thoroughly with water, ethanol and diethyl ether and dried under vacuum to provide the desired product (calculated (M+H)<sup>+</sup>: AlQF, 742.69; AlQF2, 1024.95; found (M+H)<sup>+</sup>: AlQF, 742.10; AlQF2, 1024.36). The quantum yield of these complexes was determined using quinine sulfate in dilute H<sub>2</sub>SO<sub>4</sub> aqueous solution as standard. The luminescence quantum yield of the complexes is calculated using the following equation:

$$\phi_u = \left(\frac{A_s}{A_u} \frac{I_u}{I_s}\right) \left(\frac{\eta_u}{\eta_u}\right)^2 \phi_s \tag{1}$$

where  $\phi_u$  and  $\phi_s$  are the emission quantum yield of the complex and standard,  $A_u$  and  $A_s$  are the absorbance of sample and standard, whereas  $I_u$  and  $I_s$  represent the areas under the corrected spectra of the sample and standard respectively.  $\eta_u$  and  $\eta_s$  are the respective refractive index of the solvents used to prepare the samples and the standard respectively.

Spectrofluorometric titrations were performed by preparing solutions of the ligands (ca  $2.5 \times 10^{-5}$  M) by appropriate dilution from stock solutions. Titrations were then performed by adding increasing amounts (20 µL) from a stock solution of Al<sup>3+</sup> ions in methanol. Solution lifetime measurements were obtained using a TimeMaster fluorescence lifetime spectrometer (Photon Technology International, NJ, USA). Excitation was at 380 nm using an LED. The measured transient signals were fit to a multiexponential function and the goodness of fit was judged from the value of the reduced chi-squared ( $\chi^2$ ). In all the experiments a quartz cell of 1 cm was used to hold the sample and all measurements are conducted at 23 ± 1 °C.

### Computational details

The ground state geometries ( $S_0$ ) molecular structures of AlQF and AlQF2 were optimized by the *ab initio* Hartree–Fock (HF) method and the density functional theory (DFT) method using the B3LYP (Becke-three parameter hybrid exchange functional [41] combined with the Lee–Yang–Parr correlation function [42]). In all cases the 6-31G(d) basis set usually employed for the geometry optimization of AlQ complexes was sued. This basis set was reported to be sufficient to estimate the various parameters of AlQ complexes [24]. On the other hand, the first excited state geometry ( $S_1$ ) molecular structure was optimized by the single configuration interaction (CIS) [43], with 3-21G(d) basis set.

To calculate estimates of the electronic transition energies, which include some account of the electron correlation, we used the time-dependent density functional theory (TD-DFT) together with the hybrid B3LYP level of theory and using 6-31G(d) basis set. Emission energies were obtained considering the CIS optimized structures of the excited state.

All of the above calculations were performed using *Gamess-US* program [44,45]. To calculate the molecular orbital contributions of various groups and atoms the program *GaussSum* [46] was used. This program was further used to determine the contribution of

the exited state configurations to the electronic transitions and to create the spectra by convolution of molecular orbitals.

### **Results and discussion**

### Synthesis

5,7-Dibromo-8-hydroxyquinoline **1a** (Scheme S1, Supplementary information) was the starting material of the synthesis of the new ligand. Protection of hydroxyl group was carried out using chlorobenzyl to give **2a** and then the ligand underwent Suzuki cross coupling reaction with *p*-fluorophenylboronic acid to give **3a**. Deprotection of the new ligand gave **4a**. The structure of the new ligand was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR. The aluminum complexes of 8-HQ and its derivatives were prepared in methanol.

### Photopysical properties

The absorption spectra of the synthesized ligands **4a** and **4b** and their corresponding aluminum(III) complexes AlQF and AlQF2 were obtained in methanol (each at concentration of  $2.0 \times 10^{-5}$  M) at room temperature and are shown in Fig. 1. On the other hand, the emission spectra of the ligands ([ligand] =  $3.0 \times 10^{-6}$  M) and their corresponding complexes ([complex] =  $5 \times 10^{-7}$  M) are presented in Fig. 2. The photophysical data for absorption and emission are collected in Table 1. The main features of the absorption spectra are the strong energy bands around 205 and 250 nm assignable to  $\pi$ - $\pi$ \* transitions. Moreover, the spectra exhibit a broader lower energy band centered at 333 and 326 nm for **4a** and **4b** respectively.

Upon chelating both ligands to Al(III) ions the bands at 250 were red shifted. Additionally a remarkable red shift was observed for the lower energy bands for both ligands following complexation. These observations are characteristics of complexes of quino-late ligands with metal ions such as Al(III), In(III) and Zn(II) [8,18].

The luminescence spectra of ligands and their respective aluminum complexes recorded in methanol at room temperature are shown in Fig. 3. Both complexes exhibit green emission centered at 525 and 530 nm for AlQF and AlQF2 respectively. A slight red shift in the emission maximum was observed by the second substitution of 4-fluorophenyl group at C7, which is accompanied by a significant increase in the quantum yield (Table 1). Furthermore, the emission maximum of AlQF and AlQF2 are red shifted by 9 and 14 nm compared to the parent compound AlQ (516 nm in methanol). Attachment of an aryl group to the parent qunioline ligand results in an extension of the conjugation leading to enhanced quantum efficiency that is almost doubled when a second aryl substituent was placed at C7 of the phenoxide side (Table 1). It is well known that absorption to S<sub>1</sub> and fluorescence involve the same electronic states, therefore, for molecular systems with large extinction coefficients a higher fluorescence is usually expected and as a result high quantum yields are obtained for these systems [12].

Titration of **4a** and **4b** with Al(III) ions in methanol are presented in Fig. 3. It is clear from these figures that with increasing amounts of Al(III) ions in the solution a green signal starts to grow at 530 nm and 525 nm for **4a** and **4b** respectively. These titration curves are also characterized by the presence of clear isoemissive points at 462 for AlQF2 and less obvious isoemmisive points for AlQF at around 400 nm and 465 nm. The presence of isoemissive points indicates the presence of two or more species in the solution, such as the complex and the free ligand. We further investigated the stoichiometry of complexation using the continuous variation method. The molar ratio of Al(III):ligand of the predominant complex was found to be 1:3 for AlFQ and AlQF2.



Fig. 1. UV–Visible absorption spectra of  $2.0 \times 10^{-5}$  M (1) 4a (2) 4b (3) AlQF (4) AlQF2 in methanol.

### DFT calculations

To have a further insight into the structure and properties of the prepared complexes the electronic structure of these complexes



**Fig. 2.** Fluorescence spectra of: (a) (1)  $5 \times 10^{-7}$  M AlQF (2)  $3 \times 10^{-6}$  M 4a (b) (1)  $5 \times 10^{-7}$  M AlQF2 (2)  $3 \times 10^{-6}$  M 4b in methanol (1) Emission spectra (1') Excitation spectra.

were investigated by the time-dependent density functional theory (TD-DFT). The ground state geometry of mer-AlQF and mer-AlQF2 complexes are computed at the HF/6-31G(d) and B3LYP/6-31G(d) levels of theory. The optimized geometries of both complexes obtained at B3LYp/6-31G(d) level of theory (Fig. S2, supplementary information). The labels A, B, and C are used to distinguish the three quinoline ligands attached to the central aluminum ion. Table 2 presents some selected parameters of the optimized geometries of these complexes together with the parent AlQ which is presented here for comparison purposes. The adequacy of the theoretical method was checked by comparing the parameters obtained for AlQ with those reported in the literature and with the experimental X-ray crystallography data [32,47]. It is evident from these results that 4-fluorophenyl substituents at C5 and C7 exerted only slight changes on bond angles and bond lengths. However, we observed a greater effect on bond lengths especially for Al–N upon substitution of another aryl group at C7. It has been reported that there is a significant degree of coplanarity between planes of quinoline group and the aryl substituent at C5 [6]. This in turn results in the decrease of the degree of conjugation between the quinoline group and the arvl substituent and as a consequence the efficacy of the electronic interaction between the substituent and the rest of the complex is reduced. Our DFT optimized structures exhibited dihedral angles of 55° for aryl substituents at C5 which is in line with the previously reported values for ligands of the same kind [6,12]. However, the aryl substituent at C7 exhibited a dihedral angle of 33° with the quinoline group. This result indicates that the decreased coplanarity for the substituent at C7 lead to enhanced electronic communication with the parent quinoline group.

Examination of the frontier molecular orbitals (FMOs) (Fig. S3, Supplementary information) has clearly shown that both complexes exhibit electron distribution similar to the parent AlQ

Table 1				
Summary of photophysical	properties of 4a,	4b and the	eir Al- comple	exes. <sup>a</sup>

Compound	$\lambda_{abs}$ (nm)	$\lambda_{\rm em}$ (nm)	$\Phi_F$	$\tau_F(ns)$
4a	204, 243, 328	414	-	-
4b	204, 259, 333	416	-	-
AlQF1	204, 259, 377	525	0.353	$9.9 \pm 0.2$
AlQF2	204, 274, 388	530	0.702	$14.9 \pm 0.1$

<sup>a</sup> AlQF1, Al-4a complex; AlQF2, Al-4b complex.



**Fig. 3.** Titration of  $5 \times 10^{-5}$  M of (a) 4b (b) 4a with Al<sup>3+</sup> showing growth of the green emission in methanol; [Al<sup>3+</sup>] =  $0-20 \times 10^{-6}$  M.

Table 2

Selected parameters of HF/6-31G(d), B3LYP/6-31G(d) and CIS/3-21G(d) optimized geometries of ground and excited electronic states.

$R(\text{\AA})/\phi(^{\circ})$	HF		B3P		CIS	CIS		
	AlQF1	AlQF2	AlQF1	AlQF2	AlQF	AlQF2		
$\begin{array}{c} Al-N_a\\ Al-N_b\\ Al-N_c\\ Al-O_a\\ Al-O_b\\ Al-O_c\\ N_b-Al-N_c\\ N_a-Al-O_c\\ \end{array}$	2.097 2.146 2.063 1.826 1.854 1.860 171.0 171.7	2.090 2.147 2.072 1.859 1.868 1.871 170.3 171.4	2.084 2.128 2.063 1.852 1.880 1.889 171.1 172.6	2.070 2.113 2.059 1.859 1.885 1.883 170.1 172.3	2.002 2.094 2.098 1.892 1.850 1.847 171.2 172.3	2.069 2.101 2.084 1.873 1.872 1.852 171.3 169.0		
$O_a$ -Al- $O_b$ $\Phi_1$ $\Phi_2$	164.3 53	165.4 52 33	166.6 52 -	166.5 53 33	166.5 52	165.6 51 24		

complex [20,21,29,30]. As expected all MOs are ligand centered and without significant contribution from the central metal ion as has been observed previously [21,22,29,30]. Inspection of the highest occupied molecular orbital (HOMO) reveals that the aryl substituents at C5 and C7 have considerable contribution to these orbitals, however, this contribution is absent in case of LUMO orbitals. To evaluate the role of the aryl substituents in the electronic structure of these complexes we further calculated the contributions from various regions of the complexes at B3LYP/6-31G(d) level using methods reported previously [22]. The results are shown in Tables 3 and 4 for AlQF and AlQF2 respectively. As expected

HOMO orbitals are generally localized on the phenoxide side of the ligands, whereas contribution to LUMO orbitals originate from the pyridyl and the phenoxide groups with the former being the major contributor. Interestingly, the aryl substituents contribute significantly to HOMO orbitals. In the complex AlQF the aryl substituent at C5 constitutes 11%, 12% and 13% of HOMO, H - 1 and H – 2 orbitals respectively. A higher contribution of aryl substituent at C7 to HOMO orbitals (15-20%) was observed for the disubstituted ligands compared to the contribution of the aryl substituents at C5. It is evident from these results that the smaller dihedral angle between the aryl substituent at C7 and the quinoline moiety allows for higher electronic communications between the substituents and the rest of the molecule. It is also observed that the involvement of these substituents increases from HOMO to H - 2 and even a stronger participation was observed for inner MOs reaching 98% in H - 6 and L + 6.

We further investigated the electronic transitions by TD-DFT calculations using B3LYP/6-31G(d) approximation which have been reported previously to adequately simulate the absorption and emission spectra of aluminum and gallium complexes [12,20,25]. The computed electronic data are presented in Tables 5 and 6. For both complexes the calculations show that contribution to low energy absorptions involve the same molecular orbital profiles. The most intense transitions are from HOMO to L + 1 and L + 2 and from H - 2 to LUMO in both cases. On the other hand, the major contribution to the lower energy emission at 547.8 nm for AlQF involves a HOMO  $\rightarrow$  LUMO transition as shown in Table 6. For AlQF2 the emission at 558.2 nm receives contributions from  $HOMO \rightarrow LUMO$  and  $HOMO \rightarrow L + 1$  transitions. The shift in absorption and emission wavelengths has been well predicted by the theoretical TD-DFT calculations. Additionally, the calculated emission wavelengths are in good agreement with the experimentally obtained values. It is well documented in the literature that the electronic  $\pi - \pi^*$  transitions in AlQ and analogue complexes are localized on the quinoline ligands. These transitions are predominantly from a phenoxide donor to a pyridyl acceptor part of the ligand. Calculations have shown that substitution of 4-fluorophenyl groups caused red shift in emission wavelength relative to the parent AlQ complex. Furthermore, using the TD-DFT method an additional 10 nm red shift was predicted when another 4-fluorophenyl group is attached to C7. This is in good agreement with the experimental results where the shift obtained was about 5 nm. Nonetheless, the TD-DFT method was not able to predict the enhanced quantum yield as can be seen in Table 6. It has been reported in the literature using theoretical and experimental results that fluorine substituents at C5 and C7 of the quinoline ligand produce complexes that exhibited slight red shift compared to the parent AlQ complex contradicting the expectations.

From the energy level diagram of AlQ, AlQF and AlQF2 (Fig. S4, Supplementary information) it is clear, for both complexes, that HOMO energy is only slightly affected by substituents at C5 and C7, whereas the LUMO was stabilized in both cases especially for AlQF2 where the LUMO exhibited greater decrease in energy. Unexpectedly, these results are different than those obtained experimentally for complexes with electron withdrawing aryl substituents at C5 [5,6]. In these literature, it was reported that substitution of an aryl withdrawing moiety at C5 have tuned the emission color of the complexes by affecting the energy of HOMO while keeping the LUMO energy almost constant as determined by electrochemical methods.

OLEDs materials are expected to generate a strong electroluminescence due to the efficient electron-hole combination. This phenomenon accompanies injection of electrons from the cathode into the LUMO orbitals while the holes are injected into the HOMO orbitals. Enhancing the electron injection efficacy can be achieved by lowering of the LUMO energy. Generally vertical ionization

Table 3 Molecular orbital components of AIFQ (%) obtained at B3LYP/6-31G(d,p).

Orbital	Energy (eV)	Phenol A	Phenol B	Phenol C	Pyridine A	Pyridine B	Pyridine C	Phenf A	Phenf B	Phenf C	Al
L + 2	-1.52	21	6	2	52	14	4	1	0	0	0
L + 1	-1.61	7	18	3	18	43	7	0	1	0	0
LUMO	-1.83	0	4	22	0	12	57	0	0	1	0
HOMO	-4.99	69	9	0	9	1	0	11	1	0	0
H – 1	-5.18	9	66	0	1	9	1	2	12	0	1
H-2	-5.27	1	0	74	0	1	10	0	0	13	0
L + 1	-1.61	7	18	3	18	43	7	0	1	0	0

Table 4 Molecular orbital components of AIF2Q (%) obtained at B3LYP/6-31G(d,p).

	Energy (eV)	Phenol A	Phenol B	Phenol C	Pyridine A	Pyridine B	Pyridine C	Phenf 5A	Phenf 5B	Phenf 5C	phenf 7A	Phenf 7B	Phenf 7C	Al	Al
L+2	-1.74	22	5	2	53	10	3	1	0	0	2	1	0	0	0
L+1	-1.84	5	19	6	22	34	7	0	1	0	1	3	1	0	1
LUMO	-2.06	0	4	22	0	11	55	0	0	1	0	1	3	0	3
HOMO	-5.01	58	7	0	8	1	0	7	1	0	15	2	0	1	0
H – 1	-5.21	6	56	1	1	8	1	1	8	0	2	17	0	0	0
H-2	-5.3	0	0	59	1	0	9	0	0	8	0	0	20		20

### Table 5

Calculated absorption wavelengths ( $\lambda$ ), oscillator strengths (f) and major contribution at TD-B3LYP/6-31G(d) level of theory using HF/6-31G(d) geometry for AlQF and AlQF2.

λ (nm)	$f_{calc}$	Major contribution
ALOF		
433.88	0.0193	HOMO $\rightarrow$ LUMO (91%)
422.20	0.1151	HOMO $\rightarrow$ L + 1 (60%), HOMO $\rightarrow$ L + 2 (24%)
413.11	0.0487	$H - 2 \rightarrow LUMO (81\%)$
411.25	0.0211	$H - 1 \rightarrow LUMO (73\%)$
387.43	0.0146	$H - 1 \rightarrow L + 1$ (71%)
375.17	0.0119	$H - 2 \rightarrow L+ (97\%)$
314.51	0.0207	HOMO $\rightarrow$ L + 3 (91%)
ALOF2		
465.80	0.0211	HOMO $\rightarrow$ LUMO (92%)
447.42	0.0707	HOMO $\rightarrow$ L + 1 (56%), HOMO $\rightarrow$ L + 2 (21%)
439.57	0.0606	H – 2 → LUMO (80%)
438.40	0.0201	HOMO $\rightarrow$ L + 2 (70%), HOMO $\rightarrow$ L + 1 (21%)

### Table 6

Calculated emission wavelengths ( $\lambda$ ), oscillator strengths (f) and major contribution at TD-B3LYP/6-31G(d) level of theory using CIS/3-21G(d) geometry for AlQF and AlQF2.

λ (nm)	$f_{calc}$	Major contribution
ALOF		
547.8	0.0730	$HOMO \rightarrow LUMO (96\%)$
424.2	0.0275	$H - 1 \rightarrow L + 1 (90\%)$
AQF2		
558.2	0.0650	HOMO $\rightarrow$ LUMO (61%), HOMO $\rightarrow$ L + 1 (37%)
542.5	0.0790	$H - 2 \rightarrow LUMO (76\%), H - 2 \rightarrow L + 1 (18\%)$

potential (VIP) and electron affinities (VEA) are used to evaluate the energy barriers associated with the injection of electrons and holes into OLEDs. These parameters can be calculated using the DFT methods using the following equations:

$$VIP = E_N^+ - E_N^0$$
(2)  
$$VEA = E_N^0 - E_N^-$$
(3)

where  $E_N^+$ ,  $E_N^-$ , and  $E_N^0$  are the total energy of the cationic, anionic and neutral states calculated at the optimized neutral geometry, respectively. The calculated values of VIP and VEP as well as the other descriptors such as the hardness ( $\eta$ ), the chemical potential and the global electrophlicity index ( $\omega$ ) are presented in Table 7. It is apparent from these results that VEA is greatly affected by substitution of aryl groups at C5 and C7 position of the quinoline ligand compared to VIP which is less affected. Substitution of a 4-fluorophenyl group at C5 resulted in a 0.3 eV decrease in VEA compared to the parent molecule, AlQ. Interestingly, a further 0.33 eV decrease in VEA was observed when a second substituent was placed at C7 of the quinoline ligand. It can be inferred from these results that the di-substitution of electron withdrawing aryl groups at C5 and C7 positions could be an effective way to improve the electron injection abilities of AlQ complexes.

Chemical hardness ( $\eta$ ) and global electrophilicity index ( $\omega$ ) are customarily used to describe the chemical stability and reactivity of chemical species. These descriptors are calculated by the following equations [33]:

$$\eta = \frac{\text{VIP} - \text{VEA}}{2} \tag{4}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{5}$$

The results in Table 7 reveals the fact that hardness of the aluminum complexes included in this study decrease upon substitution with the highest hardness value obtained for the parent molecule. The global reactivity index ( $\omega$ ) measures the electrophilic power of the molecule. The results shown in Table 7 clearly indicate that  $\omega$  increases with substitution at C5 and C7 positions. Therefore, this global electrophilicity index can be utilized to assess the electron injection properties of OLEDs.

Table 7

Energy of the lonization potential, electron affinity, global hardness, global electrophilicity index and other descriptors.

Parameter (eV)	AlQ	AlQF	AlQF2
Ionization potential (VIP)	6.32	6.18	6.10
Elecrn Affiniy(VEA)	0.47	0.77	1.10
Hardness $(\eta)$	2.93	2.71	2.50
Chemical potential $(\mu)$	-3.40	-3.46	-3.60
Electronegativity $(\chi)$	3.40	3.48	3.60
Global electrophilicty index ( $\omega$ )	1.97	2.23	2.60

### Conclusion

We have developed new 4-fluorophenyl substituted derivatives of 8-hydroxyguinoline and their aluminum complexes. The absorption and emission spectroscopy properties of the aluminum complexes of the new ligands were further studied. A higher quantum yield was obtained for both complexes compared to the parent tris(8-hydroxyquinolinolate)aluminum(III) with AlQF2 exhibiting the highest quantum yield. On the basis of their photophysical properties these complexes can be considered as efficient green light emitters. Moreover, using DFT methods the ground state structure was calculated using the B3LYP/6-31G(d) level of theory. On the other hand the first excited state was optimized by CIS methods at 3-21G(d) level of theory. The aryl substituents were predicted to contribute significantly to the HOMO orbitals. Additionally, using TD-DFT methods the predicted emission and absorption wavelengths were in good agreement with the experimental results.

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### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.08.055.

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