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New Alq_3 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 Alq_3 derivatives are shifted according to the electronic properties of the substituents at position-4. Results from differential scanning calorimetry (DSC) investigations of the new Alq_3 derivatives indicate that the complexes **9** and **10** are non crystalline and have higher transition glass temperatures than the parent Alq_3. 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.

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]

Alq_3 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 Alq_3 through modulation of HOMO levels by synthesizing differently substituted 8-hydroxyquinolines in which the substitutions are introduced to the phenoxide ring[14] (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 Alq_3 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-workers[19] have introduced the strong electron withdrawing $-SO_2NR_2$ group at C-5 of the 8-hydroxyquinoline and EL investigations of the resulting Alq_3 derivative revealed that the emission wavelength was significantly blue shifted (λ_{PL}=480 nm) compared with the emission wavelength of the parent Alq_3 (λ_{PL}=514 nm). 8-Hydroxyquinolines with alkoxymethyl, aminomethyl and carbazole substituents at C-5 have been also prepared and the photophysical properties of their Alq_3 derivatives have been studied.[20–23]

Difluorinated Alq_3 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 Alq_3 derivatives for OLED applications are still rare. Tuning the emission of Alq_3 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 Alq_3 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]

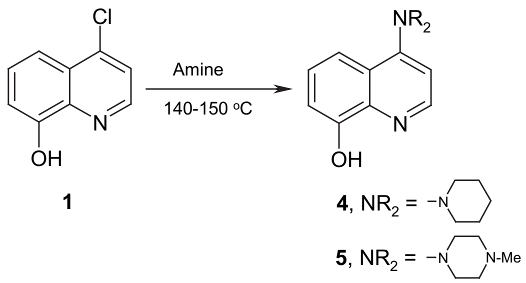
The new Al complexes are equipped with chloro, pyrazolyl, and 3-methylpyrazolyl groups as electron withdrawing substituents, and piperidinyl and *N*-methylpiperazinyl groups as electron donating substituents at C-4 of the 8-hydroxyquinolate ligand. The photoluminescence emission wavelengths of the new 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 Alq_3 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 Alq_3 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 Alq_3 as emitters. CsF/Al was used as the cathode due to its high efficiency.[8,46]

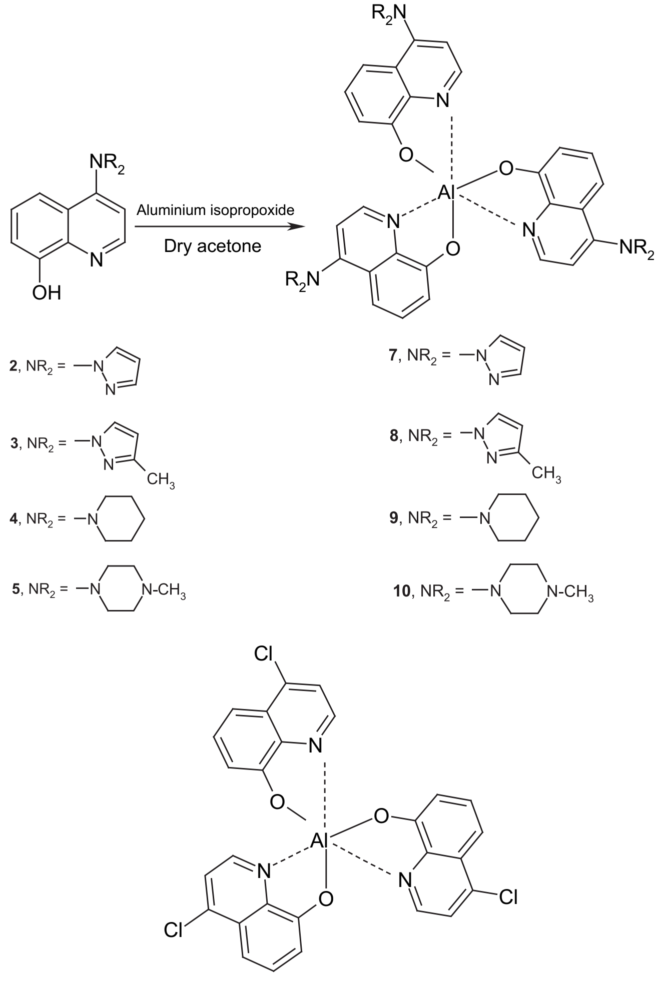
2. Results and discussion

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 ^{13}C 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 Alq_3 derivatives were characterized by ^1H NMR and ^{13}C NMR spectroscopy, IR and HRMS. The ^1H NMR spectra at room temperature of the new complexes showed the presence of meridinal 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 Alq_3. The blue shifted Alq_3 derivatives **9** and **10** show completely different DSC behaviour than the complexes **6**–**8** and the parent Alq_3 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 indicates that complexes **9** and **10** are amorphous Alq_3 derivatives with higher transition glass temperatures than the parent Alq_3 (T_g=174 °C),[35] which may indicate higher stability for the glass phase. The higher T_g values of materials **9** and **10** could be partly attributed to their higher molecular weights than the parent Alq_3.[27,32] The amorphous morphologies of complexes **9** and **10** are also confirmed by powder X-ray analysis (see p. 36 in SI). No sharp signals could be detected in the powder X-ray diffractograms of complexes **9** and **10** and only broad amorphous halos were observed.

We attribute the amorphous property to an increase in the number of conformers together with non-planar structures.[27–29] To the best of our knowledge, the complexes **9** and **10** are the first amorphous Alq_3 derivatives reported so far.

2.2. Photoluminescence measurements

Photophysical properties of the new Alq_3 derivatives correlate well with the electronic properties of the substituents at position-4 of the quinolate ligand. The emission wavelengths can efficiently be tuned by varying the electronic properties of the substituents at C-4 of the substituted ligands. The photoluminescence characteristics of the new Alq_3 derivatives are shown in Figure 1.

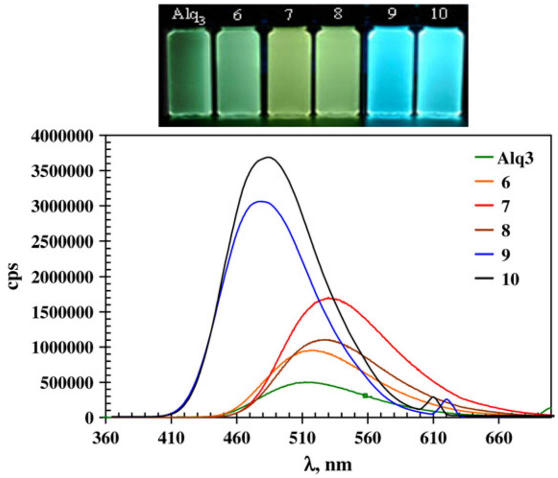


Figure 1. The photoluminescence emission of Alq_3 and its derivatives in chloroform.

Although electron-withdrawing chloro, pyrazolyl and 3-methylpyrazolyl substituents caused a slight red shift of 19 nm compared with the parent Alq_3 (λ_{PL}=512 nm in chloroform), their emissions are still in the green region of the visible light. Electron-donating piperidinyl and *N*-methylpiperazinyl groups caused a relatively strong blue shift of about 35 nm compared with the parent Alq_3. Also, compared with the parent Alq_3 the optical band gap energies are lower in the complexes with electro-withdrawing chloro, pyrazolyl and 3-methylpyrazolyl substituents at C-4 of the ligand, while the optical band energies are higher in the complexes with electron donating piperidyl and *N*-methylpiperazinyl substituents at C-4 of the ligands.

The UV–vis absorption, PL emission measurements of all the new aluminum complexes were made in chloroform and the results are summarized in Table 1. The relative PL quantum yields of the new complexes were calculated using the relation used by Velapoldi et al.[42] Because the calcd relative PL quantum yields of complexes **7**, **9**, and **10** (2, 2.1 and 3.38, respectively) are higher than the quantum yield of parent Alq_3 (1.00), complexes **7**, **9**, and **10** were investigated further as potential emitters in OLED devices.

Table 1
The photophysical and thermal properties of complexes **6**–**10** and Alq_3

Complex	λ_{ab} (ε)[a]	λ_{em}[b]	Φ_{PL}[c]	Optical band gap[d]	T_m[e] (°C)
Alq_3	389 (6.0×10^3)	512	1.00	3.19	412
6	399 (7.4×10^3)	518	1.46	3.11	378
7	407 (9.9×10^3)	535	2.02	3.05	403
8	405 (1.4×10^4)	534	0.91	3.06	353
9	374 (1.4×10^4)	477	2.1	3.32	Nd (196)[f]
10	377 (1.1×10^4)	485	3.38	3.29	Nd (216)[f]

[a] Absorption maximum (nm) and molar absorptivity (L mol^{-1} cm^{-1}) in brackets.
[b] Photoluminescence emission maximum (nm) for 20 μM of sample in chloroform, the absorption maximum was used as the excitation wavelength.
[c] Relative PL quantum yield calculated from the relation used by Velapoldi et al. and giving a quantum yield of 1.00 to Alq_3.[42]
[d] Estimated from the UV–vis spectra by using $E=hC/\nu$.
[e] Melting points (°C).
[f] No melting endotherms were detected and between brackets are the T_g values in °C.

2.3. The electroluminescent measurements

To illustrate the efficiency of the new Alq_3 derivatives as emitters in OLED devices, low cost OLED devices with the configuration ITO/PVK/Alq_3 derivative/CsF/Al were fabricated from the complexes **7**, **9**, and **10** and commercial Alq_3. The hole transporting material, PVK, was spin coated on ITO glass. Due to the low solubility of the parent Alq_3, all the tested Alq_3 derivatives and commercially Alq_3 were thermally evaporated over the spin coated hole transporting layer in order to maintain a uniform emitter application procedure during the device fabrication. CsF and Al are then thermally evaporated on top of the Alq_3 derivative. The resulting EL spectra of the selected complexes from OLEDs with the previously mentioned configuration are shown in Figure 2.

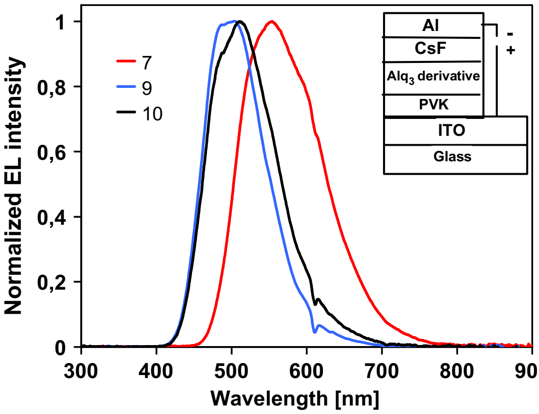


Figure 2. Normalized EL spectra of the selected complexes (**7**, **9**, and **10**), the inserted picture shows the device configuration.

The EL emission spectra for the three tested complexes show that, similarly to the PL emission, complex **7** has a red shifted EL emission wavelength maximum while complexes **9** and **10** have blue shifted emission wavelength maxima compared with the parent Alq_3. The more red shifted emission maxima observed in the EL spectra than the PL spectra of the three tested complexes (**7**, **9**, and **10**) could be attributed to molecular aggregation usually observed in the solid state than in the dilute solutions.[36] Figure 3 shows the luminance versus voltage of the selected complexes.

Maximum brightness values of complexes **7** and **9** are 9000 and 10,900 cd/m^2, respectively. These luminance values are about three times higher than the luminance from an identical OLED with commercial Alq_3 as emitter (3041 cd/m^2) (Table 2). Moreover the External quantum efficiencies measured from the selected

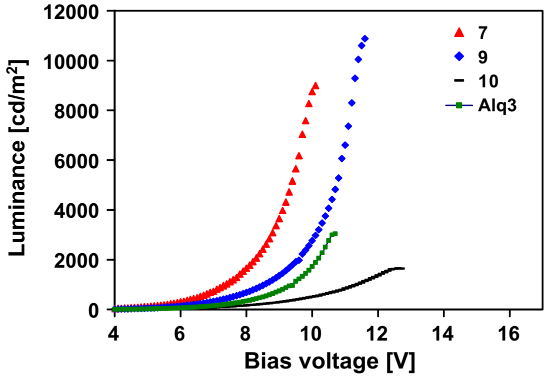


Figure 3. The luminance of the selected complexes and Alq_3 against the voltage.

Table 2
Summary of the electroluminescence measurements

Complex	λ_{EL}[a]	L[b] (cd/m^2)	η_{max}[c]%	CIE coordinates (x, y)
Alq_3	525	3041	0.46	0.28, 0.50
7	555	9000	0.57	0.41, 0.53
9	495	10,900	1.15	0.20, 0.40
10	510	1860	0.63	0.24, 0.44

[a] The electroluminescence emission maximum (nm).
[b] The luminance in cd/m^2.
[c] The external quantum efficiency of the device.

complexes showed high values especially for complex **9** with an EQE of 1.15% while an identical device using commercial Alq_3 as emitter had an EQE of 0.46%. Figure 4 shows the high external quantum efficiencies of OLEDs with the new Alq_3 derivatives **7, 9**, and **10** as the emitters.

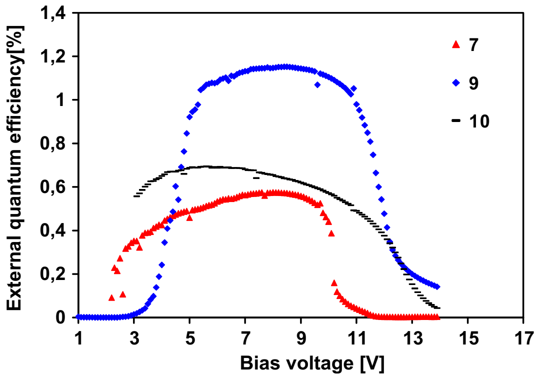


Figure 4. External quantum efficiency of complexes **7**, **9**, and **10**.

The electroluminescence data from Figures 2–4 in addition to the CIE coordinated from the EL emission spectra are summarized in Table 2.

3. Conclusion

Preparation of new ligands derived from 8-hydroxyquinoline with amino functionalities at position-4 was completed successfully in high yields and short reaction time by using solvent free synthesis in a direct reaction between 4-chloro-8-hydroxyquinoline and the proper amine. The aluminum complexes of the ligands have been prepared by the reaction between the ligand and Al isopropoxide in dry acetone. All the new complexes show higher solubilities in common organic solvents than the parent Alq_3 especially complexes **9** and **10**, which are highly soluble in alcohols, acetone, chloroform, THF and DMF.

The PL and the EL emission wavelengths of the new aluminum complexes can be tuned according to the electronic properties of the substituents at position-4. An electron-withdrawing group causes a red shift while an electron-donating group causes a blue shift compared to the parent Alq_3.

The attachment of nitrogen functionalities especially the six membered piperidyl and *N*-methylpiperizinyl saturated groups to C-4 of the 8-hydroxyquinoline nucleus, improved the solubility, thermal, morphological, PL and EL properties of the corresponding Alq_3 derivatives.

The Alq_3 derivatives **9** and **10** have higher T_g values than the parent Alq_3 and no melting endotherms could be observed in DSC measurements. A high glass transition temperature usually indicates higher glass phase stability and longer operation life time of the OLED. X-ray powder diffraction showed clearly the amorphous nature of complexes **9** and **10**. The amorphous morphology is a desired property in OLED devices because amorphous materials are able to form uniform, stable and transparent thin films during the OLED fabrication.

The electroluminescence measurements from OLED devices showed that the tested complexes **7, 9**, and **10** act as efficient emitters. Material **7** is red shifted and showed higher luminance and external quantum efficiency than the parent Alq_3 in an identical device configuration, while complexes **9** and **10** are blue shifted and showed higher external quantum efficiencies than Alq_3 in a similar device configuration. Complex **9** has the bluest shifted EL emission maximum (495 nm) among the new Alq_3 derivatives and showed the highest luminance value (10,900 cd/m^2) and an EQE of 1.15%.

4. Experimental

4.1. General

Melting points and DSC curves were determined using METTLER TOLEDO DSC821e at a heating rate of 10 °C/min. NMR analysis (^1H and ^{13}C) were performed on a Bruker DPX 200 (200 MHz) spectrometer using either $CDCl_3$ or DMSO-d_6 solutions (referenced internally to Me_4Si); *J* values are given in Hertz. IR spectra were measured on a Bruker IFS 66 spectrophotometer. TLC was performed on dry silica gel plates and developed by using chloroform/methanol mixture as the eluent. High resolution mass spectra were recorded on a Micro mass LCT spectrometer. UV absorption was measured by using a Shimadzu UV-1601 spectrophotometer. Photoluminescence measurements were made on a 2× fluoremetry device (300–700 nm) at room temperature in chloroform solutions (20 μM). Angstrom Engineering 11 source thermal deposition chamber was used for finalizing the OLED devices fabrication. Spectra were measured in a nitrogen filled glove box by using Ocean Optics HR4000 spectrometer and I-V measurements were carried out using Keithley 2400 source meter. The optical power was measured using Newport 2832C power meter.

All reagents and solvents were purchased from Sigma–Aldrich Finland and were used without further purification. Molecular sieves were used to dry the solvents. Compound **1** was prepared from the commercially available xanthurenic acid according to earlier reported procedures.[47,49]

4.2. Synthesis of 4-piperidin-1-yl-quinolin-8-ol (4)

4-Chloro-8-hydroxyquinoline **1** (0.5 g, 2.78 mmol)[47,49] and piperidine (1 mL, 11.1 mmol) were stirred in an oil bath at 140–150 °C for 3 h. After cooling to room temperature, 40 mL of water was added to the mixture. The precipitate formed was filtered and recrystallized from ethyl acetate to give the title compound as yellowish white crystals (0.6 g, 95%). Mp: 147–148 °C; IR (KBr): ν 3300, 2928, 2810 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.55–8.58 (d, *J*=5.3 Hz, 1H), 8.11 (br s, 1H), 7.32–7.48 (m, 2H), 7.09–7.14 (dd, *J*=1.4, *J*=7.6 Hz, 1H), 6.80 (d, *J*=5.0 Hz, 1H), 3.18–3.23 (t, *J*=5.6 Hz, 4H), 1.80–1.89 (quint, *J*=5.1 Hz, 4H), 1.69–1.74 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 24.85, 26.45 (2C), 53.78 (2C), 109.49, 109.72, 114.64, 124.14, 126.23, 140.09, 148.67, 153.14, 158.53. HRMS $(M+H)^+$ calcd for $C_{14}H_{17}N_2O$: 229.1341, found: 299.1338.

4.3. 4-(4-Methypiperazin-1-yl)-quinolin-8-ol (5)

The title compound was prepared by the previous procedure used for ligand **4** by reacting 4-chloro-8-hydroxyquinoline **1** (1.3 g, 7.2 mmol) and *N*-methylpiperazine (2 mL, 18 mmol) in an oil bath at 140–150 °C for 1 h. After cooling to room temperature, 30 mL of water was added to the reaction mixture. The precipitate formed was filtered, washed with water and recrystallized from ethyl acetate to give **5** (1.5 g, 88%) as yellowish crystals. Mp: 136–137 °C; IR (KBr): ν 3219, 2930, 2834 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.57–8.59 (d, *J*=5.0 Hz, 1H), 7.36–7.43 (m, 2H), 7.09–7.13 (dd, *J*=1.4 Hz, *J*=7.2 Hz, 1H), 6.85 (d, *J*=5.1 Hz, 1H), 3.27–3.32 (t, *J*=4.9 Hz, 4H), 2.68–2.73 (t, *J*=4.9 Hz, 4H), 2.42 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 46.53, 52.25, 55.40, 109.66, 109.93, 114.36, 123.89, 126.54, 140.07, 148.67, 153.24, 157.40. HRMS $(M+H)^+$ calcd for $C_{14}H_{18}N_3O$: 244.1450, found: 244.1453.

4.4. General procedures for the synthesis of aluminum complexes

4-Chloro-8-hydroxyquinoline 1 (3 equiv) was dissolved in dry acetone (25 mL) and then aluminum i*so*-propoxide (1 equiv) was added. The reaction mixture was *heated at reflux* under a nitrogen atmosphere for 24 h.

4.4.1. Al tris(4-chloro-quinolin-8-ol) ***(6)***. The specific amounts of chemicals used are: 4-chloro-8-hydroxyquinoline **1** (0.4 g, 2.22 mmol) and aluminum isopropoxide (0. 15 g, 0.73 mmol). The title complex formed gradually during the reaction as yellowish green precipitate (0.36 g, 85%). The precipitate was filtered, washed with dry acetone and dried under vacuum. Mp: 378–379 °C; IR (KBr): ν 3069, 1916, 1600 cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d_6): δ (ppm) 8.63–8.65 (d, *J*=5.2 Hz, 1H), 8.52–8.54 (d, *J*=5.2 Hz, 1H), 7.85–7.87 (d, *J*=5.2 Hz, 1H), 7.76–7.78 (d, *J*=5.2 Hz, 1H), 7.58–7.66 (m, 4H), 7.42–7.45 (d, *J*=5.2 Hz, 1H), 7.21–7.28 (m, 3H), 6.99–7.03 (d, *J*=7.8 Hz, 2H), 6.84–6.88 (d, *J*=7.8 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 109.08, 109.28, 109.46, 113.97, 114.47, 115.04, 121.76, 122.40 (2C), 128.14, 128.39 (2C), 132.30, 132.44, 132.87, 140.39 (2C), 141.07, 142.18, 144.26, 144.66, 146.89, 147.07, 147.45, 158.93, 159.29, 159.51. HRMS $(M+H)^+$ calcd for $C_{27}H_{17}N_3O_3AlCl_3$: 562.0073, found: 562.0074.

4.4.2. Al tris(4-pyrazol-1-yl-quinolin-8-ol) ***(7)***. The specific amounts of chemicals used are: 4-pyrazol-1-yl-quinolin-8-ol **2** (0.3 g, 1.4 mmol) and aluminum isopropoxide (0.095 g, 0.46 mmol), the yellowish green precipitate formed (0.27 g, 86%) was filtered and washed with cold acetone, dried under vacuum. Mp: 403–404 °C; IR (KBr): ν 3113, 3076, 2658, 1706, 1581 cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d_6): δ (ppm) 8.84–8.87 (d, *J*=5.6 Hz, 1H), 8.71–8.73 (d, *J*=5.3 Hz, 1H), 8.46–8.51 (m, 3H), 7.99 (m, 3H), 7.87–7.89 (d, *J*=5.4 Hz, 1H), 7.76–7.78 (d, *J*=5.3 Hz, 1H), 7.54–7.72 (m, 8H), 7.01–7.05 (d, *J*=7.5 Hz, 2H), 6.85–6.89 (dd, *J*=6.9, *J*=1.4 Hz, 1H), 6.7 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 108.54, 108.98 (2C), 109.04, 109.09, 109.31, 113.63, 114.09, 114.67, 115.63, 115.97, 116.06, 123.05, 123.39 (2C), 131.58 (2C), 131.77, 132.19, 132.32, 132.73, 141.95, 141.98, 142.63, 143.15, 143.23, 143.24, 143.49, 145.05, 145.41, 147.02, 147.13, 147.28, 159.02, 159.40, 159.64. HRMS $(M+H)^+$ calcd for $C_{36}H_{25}N_9O_3Al$: 658.1896, found: 658.1860.

4.4.3. Al tris{4-(3-methylpyrazol-1-yl)-quinolin-8-ol} ***(8)***. The specific amounts of chemicals used are: 4-(3-methylpyrazolyl)-8-hydroxyquinoline **3** (0.3 g, 1.33 mmol) and aluminum isopropoxide (0.09 g, 0.44 mmol), the yellow precipitate formed (0.26 g, 83%) was filtered and washed with cold acetone. Mp: 353–354 °C; IR (KBr): ν 3075, 2927, 1922, 1580 cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d_6) δ (ppm): 8.79–8.82 (d, *J*=5.6 Hz, 1H), 8.66–8.69 (d, *J*=5.4 Hz, 1H), 8.35–8.40 (d, *J*=5.2 Hz, 1H), 8.35–8.40 (m, 3H), 7.70–7.83 (m, 5H), 7.54–7.61 (m, 5H), 6.98–7.02 (dd, *J*=7.4, *J*=2.4 Hz, 2H), 6.84 (d, *J*=7.8 Hz, 1H), 6.51 (m, 3H), 2.33 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 14.17 (3C), 108.69, 108.94, 109.17, 109.33, 109.60, 113.48, 113.92, 114.52, 115.02, 115.41, 115.46, 122.79, 123.06, 123.09, 131.89, 131.95, 132.29 (2C), 132.45, 132.51, 141.93 (2C), 142.64, 143.17, 145.06, 145.34, 146.99, 147.07, 147.22, 152.88, 152.93 (2C), 153.20, 159.03, 159.40, 159.61. HRMS $(M+H)^+$ calcd for $C_{39}H_{31}N_9O_3Al$: 700.2365, found: 700.2341.

4.4.4. Al tris(4-piperidin-1-yl-quinoline-8-ol) ***(9)***. The specific amounts of chemicals used are: 4-piperidin-1-yl-quinolin-8-ol **4** (0.45 g, 1.97 mmol) and aluminum isopropoxide (0.13 g, 0.64 mmol). After 24 h, the reaction mixture was then concentrated and treated with petroleum ether, the pale yellowish precipitate formed (0.43 g, 92%) was washed with petroleum ether and dried under vacuum. IR (KBr): ν 3379, 3049, 2932, 2849, 1595 cm^{-1}. ^{1}H NMR (200 MHz, DMSO-d_6): δ (ppm) 8.34–8.37 (d, *J*=5.5 Hz, 1H), 8.25–8.28 (d, *J*=5.3 Hz, 1H), 7.24–7.34 (m, 3H), 6.55–7.04 (m, 10H), 3.20–3.22 (m, 12H), 1.65–1.66 (m, 18H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 24.81 (3C), 26.31 (6C), 53.17 (6C), 108.12, 108.21, 108.50, 108.58, 108.62, 108.82, 111.87, 112.17, 113.08, 123.42, 123.91, 123.99 (2C), 128.56, 128.75, 129.00, 141.86 (2C), 142.00, 143.42, 145.25, 145.49, 160.10, 160.25 (3C), 160.30. HRMS $(M+H)^+$ calcd for $C_{42}H_{46}N_6O_3Al$: 709.3447, found: 709.3425.

4.4.5. Al tris{4(4-methylpiperazin)-1-yl-quinolin-8-ol} ***(10)***. The specific amounts of chemicals used to prepare the title compound are: 4-(4-methylpiperazine-1-yl)-quinolin-8-ol **5** (0.6 g, 2.46 mmol) and aluminum isopropoxide (0.167 g, 0.8 mmol). The complex was precipitated by adding petroleum ether, the light yellow precipitate formed (0.56, 90%) was collected by filtration and dried under vacuum. IR (KBr): ν 3365, 2936, 2838, 2795, 2218, 1918, 1596 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.57–8.61 (m, 2H), 7.27–7.38 (m, 3H), 7.13–7.16 (d, *J*=5.6, 1H), 6.95–7.04 (m, 6H), 6.65–6.72 (m, 2H), 6.52–6.54 (d, *J*=5.6 Hz, 1H), 3.25–3.37 (m, 12H), 2.63–2.65 (m, 12H), 2.37–2.39 (m, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 46.48 (3C), 51.70 (6C), 55.38 (6C), 108.43 (2C), 108.51, 108.71, 108.74, 108.76, 112.11, 112.44, 113.30, 123.30, 123.73, 123.83, 128.96, 129.18, 129.44, 141.20 (2C), 141.78, 143.44, 145.28, 145.55, 159.28, 159.35 (2C), 159.45, 160.06 (2C). HRMS $(M+H)^+$ calcd for $C_{42}H_{49}N_9O_3Al$: 754.3774, found: 754.3776.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.09.095.

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