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Synthesis of 5-alkoxymethyl- and 5-aminomethyl-substituted 8-hydroxyquinoline derivatives and their luminescent Al(III) complexes for OLED applications

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Abstract—Several 5-alkoxymethyl- and 5-aminomethyl-substituted 8-hydroxyquinolines were synthesised. Their coordination complexes with Al(III) were also synthesised. These complexes are soluble and stable in common organic solvents and show green luminescence with high quantum yields.

The synthesis and implementation of new charge-transporting and emissive materials in organic light emitting devices (OLEDs) has afforded much fundamental information and has resulted in greatly enhanced quantum efficiency, brightness and stability. Tris-(8-hydroxyquinoline) aluminium (**AlQ_3**), an efficient green electroluminescent material, was first used as an electron transporter and photon emitter in organic light emitting devices by Tang and VanSlyke.[1] Since then it has been a workhorse material for use in OLED applications.[2] **AlQ_3** is a spherically shaped molecule with distorted octahedral geometry, where the 8-hydroxyquinoline ligands surround the Al(III) ion. The molecule has low photoluminescence (PL) quenching in the solid state, good electron mobility and good stability against recrystallisation as an amorphous thin film. Many researchers have attempted the discovery of new and improved organic materials based on 8-hydroxyquinoline for OLEDs.[3] The use of **AlQ_3** with various dyes as dopants shows substantial promise in the development of new light sources of different colour. Though **AlQ_3** is used as a good electron transporter in single and bi-layer devices, it has to be vapour deposited for thin film formation. Our aim here was to synthesise materials, which could be easily spin-castable from organic solution. This could be a gentler process and might also retain the molecular features of the material.

Keeping this in mind, we have synthesised a family of 8-hydroxyquinoline derivatives by substituting at the 5-position. These molecules were designed to have high solubility in many organic solvents and to serve the purpose of spin-coating. Their photoluminescence properties in solution have been investigated.

The ligands were designed in order to achieve better solubility without affecting the beneficial spectroscopic and luminescence properties. The solubility was enhanced by attaching a functional group to the ligand. The ligands reported here have aromatic groups attached at the 5-position through an $-OCH_2-$ or $-NCH_2-$ as the link. The $-CH_2-$ group ensures minimal effects on the aromatic properties of the ligand, irrespective of the group substituted.

5-Chloromethyl-8-hydroxyquinoline hydrochloride **1** was synthesised as reported earlier by the reaction of 8-hydroxyquinoline with formaldehyde and concentrated HCl.[4] Condensation of **1** with an excess of appropriate alcohols or amines in the presence of $NaHCO_3$ gave the corresponding 5-substituted products (Scheme 1). These ligands were purified by crystallisation from appropriate solvents to give 50–60% yields. The compounds were characterised by ^1H NMR, ^{13}C NMR, ESI-MS and elemental analysis.[5] The mass spectra of **2**, and **3** exhibited intense peaks at 301.8 and 302.07

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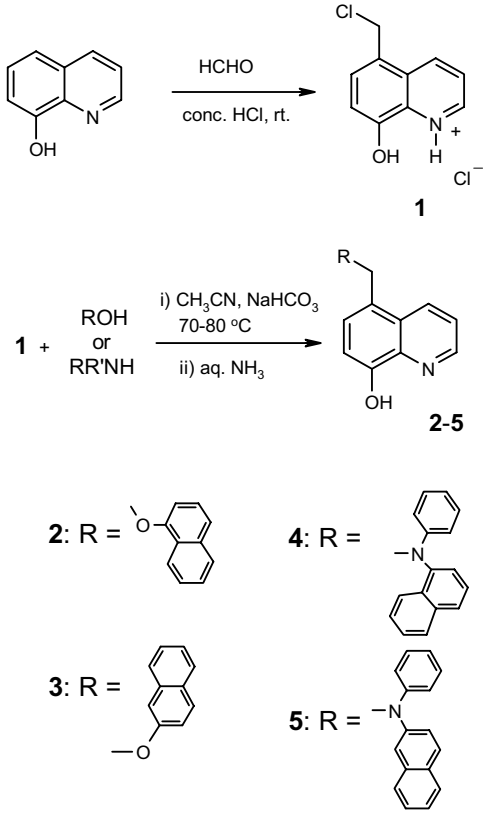
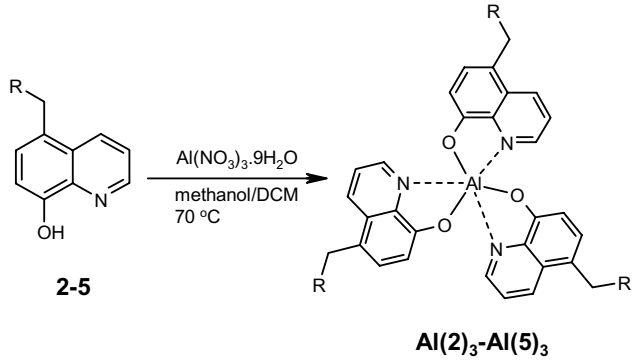


Scheme 1. Synthesis of ligands **2**–**5**.

assigned to M^+ and $(M+H)^+$ whereas **4** and **5** gave peaks at 377.2 and 377.47 corresponding to $(M+H)^+$.

Reaction of these ligands with $Al(NO_3)_3 \cdot 9H_2O$ in the presence of Na_2CO_3 in MeOH/DCM (9:1) solution afforded yellow fluorescent materials in quantitative yields, which were recrystallised from MeOH/$CHCl_3$ (~7:3) (Scheme 2). The structures of the Al(III) complexes, **Al(X)$_3$** (**X** = **2**–**5**) were confirmed by ^{1}H NMR, ESI-MS spectra and elemental analysis.[6] Complexes **Al(2)$_3$** and **Al(3)$_3$** showed peaks at 950.59 and 950.6 corresponding to $(M+Na)^+$ and 928.13 and 928.06 corresponding to M^+, respectively. Peaks were found at 1153.4 (M^+) and 1176.4 $(M+Na)^+$ for **Al(4)$_3$** and **Al(5)$_3$**, respectively. The aluminium complexes in princi-



Scheme 2. Synthetic route for complexes **Al(2)$_3$**–**Al(5)$_3$**.

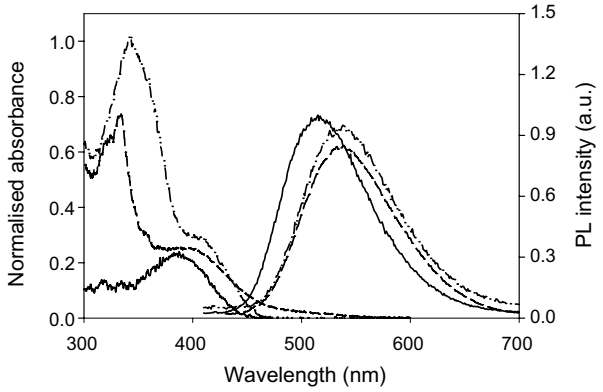


Figure 1. Absorption and emission spectrum of **AlQ$_3$** (solid line), **Al(3)$_3$** (dash-dotted line) and **Al(4)$_3$** (dashed line) in DCM solution. Emission spectra recorded on excitation at 390 nm at 298 K.

ple could exist in two different isomeric forms, *mer* (meridianal) and *fac* (facial). Evidence for such isomeric forms was provided by the multiple ligand peaks seen in their ^{1}H NMR spectra.[7]

The absorption and photoluminescence (PL) spectra of the complexes were measured in DCM (Fig. 1) and the spectral data are presented in Table 1. These complexes are highly soluble in many other organic solvents and are approximately 10 times more soluble than **AlQ$_3$**.

The metal complexes (**Al(X)$_3$**) showed absorptions at 400–403 nm, which is ascribed to the π–π* transition of the metal complex, with a peak at 330–345 nm and a shoulder at around 325 nm (Fig. 1). The band at 400 nm is 16 nm red shifted compared to that of **AlQ$_3$**. The emission maxima of these complexes were at 538–540 nm, whereas **AlQ$_3$** showed PL emission at 516 nm in DCM. This red shift in both absorption and emission bands probably reflects the electron-donating effect of the substituents at the 5-position of the 8-hydroxyquinoline moiety. The similarity in emission spectra of **AlQ$_3$** and **Al(X)$_3$**, indicates that the shape and chemical properties of the substituents do not substantially affect the **AlQ$_3$**-based chromophoric core. These complexes show quantum yields 2–3 times less than that of **AlQ$_3$** (Table 1). This decreased quantum yield is also reflected in the decrease in average fluorescence lifetime (τ_f).

In summary, several novel 5-substituted 8-hydroxyquinoline derivatives were synthesised and their complexation

Table 1. Absorption and emission properties of the aluminium complexes in DCM solution

Complexes	λ_{abs} (nm)	λ_{em} (nm)	Φ_f[a]	τ_f[b] (ns)
AlQ$_3$	384, 334 (sh), 320 (sh)	516	1	16.72
Al(2)$_3$	400 (sh), 330, 325 (sh)	540	0.29	4.25
Al(3)$_3$	401 (sh), 340, 325 (sh)	539	0.28	4.05
Al(4)$_3$	402 (sh), 345	538	0.45	6.02
Al(5)$_3$	403 (sh), 340, 310	539	0.27	3.9

[a] Absolute quantum yield of **AlQ$_3$** in DCM is 0.22 Ref. 8.

[b] Average lifetime: $\tau_f = (\alpha_1\tau_1 + \alpha_2\tau_2)/(\alpha_1 + \alpha_2)$, where α_1 and α_2 are the amplitudes, and τ_1 and τ_2 are the lifetimes of two exponential decay function: $\alpha_1 e^{(-t/\tau 1)} + \alpha_2 e^{(-t/\tau 2)}$.

with Al(III) was investigated. The aluminium complexes produced were highly soluble in most organic solvents and showed green luminescence. Due to their high quantum yield and emissive nature these complexes could be good candidates for electroluminescence devices. The attachment of an aromatic *tert*-amine in complexes **Al(4)$_3$** and **Al(5)$_3$** could allow them to act as hole-transporters, electron-transporters and photon emitters for OLEDs. Detailed electroluminescent studies of these complexes are in progress.

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Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.06.089.

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5. *Typical procedure for the synthesis of ligands*. To a suspension of **1** (2 g, 8.7 mmol) in acetonitrile was added the appropriate alcohol in excess (1.2 equiv) and sodium bicarbonate (0.73 g, 8.7 mmol). The reaction mixture was heated (~70 °C) in an oil bath with stirring for 24 h. The yellow residue was filtered and then treated with dilute ammonia. The white solid formed was filtered and dried. Recrystallisation first from benzene/EtOAc (2:1) then from DCM afforded the product as a white solid. Compound **2**: (1.7 g, 50%) mp 211–213 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.68 (s, 2H, OCH_2), 6.66 (d, 1H, naphthyl, J 7.2 Hz), 6.8 (d, 1H, naphthyl, J 7.2 Hz), 7.06 (d, 2H, naphthyl, J 7.2 Hz), 7.12 (d, 1H, hydroxyquinoline, J 8.4 Hz), 7.4 (dd, 1H, hydroxyquinoline J 3.6 Hz), 7.53 (m, 2H, naphthyl and hydroxyquinoline), 8.01 (m, 2H, naphthyl), 8.27 (d, 1H, hydroxyquinoline, J 8.4 Hz), 8.79 (d, 1H, hydroxyquinoline, J 3.6 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 34.08 (*C*H_2), 108.13, 109.44, 121.64, 122.42, 123.69, 124.75, 125.12, 126.65, 126.72, 127.41, 128.37, 128.52, 129.19, 133.03, 147.46, 150.45, 150.94. ESI-MS *m*/*z* 301.8 $(M)^+$, (calcd $C_{20}H_{15}NO_2$: 301.35). Anal. calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65; found: C, 79.62; H, 5.08; N, 4.73. Compound **3**: yield = 55%; mp 223–225 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.75 (s, 2H, OCH_2), 6.78 (d, 1H, naphthyl, J 6.6 Hz), 6.91 (d, 1H, naphthyl, J 6.6 Hz), 7.05 (s, 1H, naphthyl), 7.16 (d, 1H, hydroxyquinoline, J 9 Hz), 7.3–7.4 (br, 2H, naphthyl), 7.56 (dd, 1H, hydroxyquinoline, J 4 Hz), 7.74 (d, 1H, naphthyl, J 8.5 Hz), 7.76 (d, 1H, naphthyl), 7.82 (d, 1H, hydroxyquinoline, J 8 Hz), 8.65 (d, 1H, hydroxyquinoline, J 8.4 Hz), 8.85 (d, 1H, hydroxyquinoline, J 4 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 26.58 (*C*H_2), 109.43, 116.69, 117.93, 121.73, 123.25, 123.34, 125.29, 126.28, 126.83, 127.3, 128.65, 128.87, 129.55, 132.35, 132.69, 133.85, 138.8, 147.48, 150.86. ESI-MS *m*/*z* 302.07 $(M+H)^+$, (calcd $C_{20}H_{15}NO_2$: 301.35). Anal. calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65; found: C, 79.65; H, 5.06; N, 4.72. Compound **4**: yield = 60%; mp194–196 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.75 (s, 2H, NCH_2), 6.88 (t, 2H, naphthyl, J 7.5 Hz), 6.93 (t, 2H, naphthyl, J 8.5 Hz), 7.08 (d, 1H, hydroxyquinoline, J 8 Hz), 7.15 (d, 1H, hydroxyquinoline, J 8 Hz), 7.20–7.25 (m, 3H, phenyl), 7.43 (dd, 1H, hydroxyquinoline, J 4.5 Hz), 7.47–7.58 (m, 2H, phenyl), 8.08 (dd, 1H, naphthyl, J 2.5, 2 Hz), 8.12 (dd, 1H, naphthyl, J 2.5, 2 Hz), 8.3 (d, 1H, hydroxyquinoline, J 8 Hz), 8.8 (d, 1H, hydroxyquinoline, J 4 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 34.36 (*C*H_2), 107.52, 116.39, 117.01, 120.26, 121.69, 122.77, 124.36, 125.61, 126.42, 127.04, 127.42, 128.46, 128.57, 129.33, 131.05, 132.99, 137.74, 138.77, 145.07, 147.48, 151.02. ESI-MS *m*/*z* 377.2 $(M+H)^+$, (calcd $C_{26}H_{20}N_2O$: 376.46). Anal. calcd for $C_{26}H_{20}N_2O$: C, 82.95; H, 5.35; N, 7.44; found: C, 83.02; H, 5.38; N, 7.56. Compound **5**: yield = 55%; mp 228–230 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.77 (s, 2H, NCH_2), 6.71 (d, 1H, hydroxyquinoline, J 7.5 Hz), 6.82–6.9 (m, 3H, phenyl), 6.92 (d, 1H, naphthyl, J 8 Hz), 7.2 (dd, 1H, naphthyl, J 7.5, 8 Hz), 7.4 (m, 2H, naphthyl), 7.58 (dd, 1H, hydroxyquinoline, J 4.5 Hz), 7.61 (d, 1H, hydroxyquinoline), 7.77 (dd, 1H, naphthyl, J 2.5, 2 Hz), 7.81 (d, 2H, phenyl, J 9 Hz), 7.86 (dd, 1H, naphthyl, J 2.5, 2 Hz), 8.63 (d, 1H, hydroxyquinoline, J 8 Hz), 8.87 (d, 1H, hydroxyquinoline, J 4 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 28.34 (*C*H_2), 109.51, 114.89, 116.98, 120.4, 121.56, 121.77, 123.22, 123.76, 124.11, 124.8, 125.81, 126.72, 127.32, 128.48, 128.93, 129.24, 129.43, 130.69, 132.5, 133.9, 138.92, 139.06, 144.14, 147.62, 147.73, 151.02. ESI-MS *m*/*z* 377.47 $(M+H)^+$, (calcd $C_{26}H_{20}N_2O$: 376.46). Anal. calcd for $C_{26}H_{20}N_2O$: C, 82.95; H, 5.35; N, 7.44; found: C, 83.05; H, 5.33; N, 7.42.
6. *Synthesis of complexes*. To a solution of ligand **2** (500 mg, 2.17 mmol) in methanol/DCM (9:1, 20 mL) was added $Al(NO_3)_3 \cdot 9H_2O$ (272 mg, 0.72 mmol) and Na_2CO_3 (230 mg, 2.17 mmol). The resulting mixture was refluxed for 3–4 h. After cooling, the yellow precipitate obtained was filtered off and washed with cold methanol/ethyl acetate and subsequently with water, then recrystallised from chloroform/methanol (7:3). Yield 95% (492 mg), **Al(2)$_3$**: mp >250 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.4–4.7 (br, 6H, OCH_2), 6.64, 6.75, 6.88, 6.92, 7.01, 7.07, 7.36, 7.45, 7.59, 7.7, 7.97, 8.18, 8.61, 8.74, 8.8, 9.95 (br, 36H, Ar*H*); ESI-MS *m*/*z* 950.59 $(M+Na)^+$, 928.13 (M^+), (calcd $C_{60}H_{42}N_3O_6Al$: 928). Anal. calcd: C, 77.66; H, 4.56; N, 4.53; found: C, 77.61; H, 4.59; N, 4.55. Compound **Al(3)$_3$**: yield = 92%; mp >250 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.5–4.7 (br, 6H, OCH_2), 6.43, 6.63, 7.1–7.35, 7.5–7.8 (br, 30H, Ar*H*), 8.6, 8.81, 9.01, 9.1, 9.67, 9.7 (br, 6H, Ar*H*);

ESI-MS *m/z* 950.6 $(M+Na)^+$, 928.06 (M^+), (calcd $C_{60}H_{42}N_3O_6Al$: 928). Anal. calcd: C, 77.66; H, 4.56; N, 4.53; found: C, 77.71; H, 4.55; N, 4.54. Compound **Al(4)$_3$**: yield = 97%; mp >250 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 4.55–4.75 (br, 6H, NCH_2), 6.8–6.98, 7.0–7.1, 7.15–7.25, 7.26, 7.35, 7.43, 7.52 (br, 39H, Ar*H*), 8–8.2 (br, 7H, ArH), 8.29 (d, 1H, ArH, *J* 8.5 Hz), 8.31 (d, 1H, ArH, *J* 8.5 Hz), 8.43 (d, 1H, ArH, *J* 8.5 Hz), 8.88 (d, 1H, ArH, *J* 4.5 Hz), 8.94 (d, 1H, ArH, *J* 4.5 Hz); ESI-MS *m/z* 1176.4 $(M+Na)^+$, 1153.4 (M^+), (calcd $C_{78}H_{57}N_6O_3Al$: 1153.34). Anal. calcd: C, 81.23; H, 4.98; N, 7.29; found: C, 81.30; H, 4.96; N, 7.33. Compound **Al(5)$_3$**: yield = 96%; mp >250 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 4.6–4.8 (br, 6H, NCH_2), 6.68–6.98, 7.1–7.25, 7.3–7.45, 7.5–7.7, 7.75–7.9 (br, 45H, ArH), 8.62 (d, 1H, Ar*H*, *J* 8.5 Hz), 8.66 (m, 1H, ArH), 8.76 (d, 1H, ArH, *J* 8.5 Hz), 8.87, (d, 1H, ArH, *J* 4 Hz), 8.9 (d, 1H, ArH, *J* 5 Hz), 9.0 (d, 1H, ArH, *J* 4.5 Hz); ESI-MS *m/z* 1176.39 $(M+Na)^+$, 1153.36 (M^+), (calcd $C_{78}H_{57}N_6O_3Al$: 1153.34). Anal. calcd: C, 81.23; H, 4.98; N, 7.29; found: C, 81.31; H, 5.02; N, 7.32.

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