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Synthesis and characterisation of soluble aluminium complex dyes based on 5-substituted-8-hydroxyquinoline derivatives for OLED applications

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Abstract

Some new 5-substituted 8-hydroxyquinoline derivatives and their Al(III) complex dyes ($Al(\mathbf{2})_3$–$Al(\mathbf{9})_3$) have been synthesised. The compounds were characterized by ^1H, ^{13}C, mass and elemental analysis. The aluminium complexes retain the spectroscopic properties of the parent compound, namely, tris(8-hydroxyquinolinato) aluminium (III) (AlQ_3). In dichloromethane solution, these aluminium complexes show absorption maxima in the range of 390–395 nm, strong green luminescence in the range 527–536 nm and aluminium complexes show high fluorescence quantum yield in solution and thin films. The fluorescence decay in solution as well as in thin film is fitted to biexponential with τ_{av} ranging from 3 to 9 ns. Electroluminescence (EL) of the spin-cast film of $Al(\mathbf{3})_3$ ($\mathbf{3}$ = 5-(2-ethylhexyloxymethyl)-8-hydroxyquinoline) as the emitting layer was performed and the turn-on voltage for the EL device is about 11 V.

Keywords: 8-Hydroxyquinoline derivatives; Al(III) complex dye; Photoluminescence; Electroluminescence

1. Introduction

Organic light emitting devices (OLED) have received considerable attention in recent years due to their potential application in light emitting devices and flat panel displays. The most important milestone in the luminescent organic materials research was the discovery of tris(8-hydroxyquinolinato) aluminium (III) (AlQ_3) as the electron transport material of high quantum efficiency. Much interest has been focused on the use of AlQ_3 as an electron transport and luminescent layer in a bilayer device first discovered by Tang and Van Slyke [1,2], that led to the development of stable organic electroluminescent (EL) devices, including polymer based OLEDs [3,4]. Rapid progress has been made towards developing LEDs that emit in pure red, green and blue regions of the spectrum, for a full colour and white light OLED. AlQ_3 is already credited as a pure green emitter, whereas, pure red emission by energy transfer was achieved [5a,b] by doping the AlQ_3 layer with suitable fluorescent dyes. It has been shown that an electron-donating group in the 5- or 7-position of 8-hydroxyquinoline causes a red shift in the absorption and emission spectrum; a similar effect was observed

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when an electron-withdrawing group present at 2- or 4-positions of the ring and vice versa [6a–c]. However, AlQ_3 based pure blue emission is not possible without altering the unique ligand structure. AlQ_3 films are usually prepared by vacuum deposition, which limits the area of the device and choice of substrate. Large area display devices ideally require spin-castable, highly soluble organic materials. Good quality films of AlQ_3 cannot be prepared by solution process. In recent times, attention has focused on derivatives of 8-hydroxyquinoline substituted metal complexes which were prepared and tested for OLED performance [7a,b,8,9,10a,b]. Our work was motivated towards synthesis of AlQ_3 derivatives that meets one or more of the following properties: spectroscopic and luminescence properties that are comparable to AlQ_3 dye, high solubility in organic solvents, and formation of good transparent and uniform films by spin-casting.

In this work, we report the synthesis of a family of some new soluble AlQ_3 dyes, derivatised at the 5-position of 8-hydroxyquinoline ligand, which were designed to have high solubility in many organic solvents. The spectroscopic characteristics of these molecules and the properties of spin-cast films including EL were examined and compared with similar results of AlQ_3.

2. Experimental

2.1. Materials and methods

All solvents were purchased from Qualigen and SD-fine chemicals (India). Spectroscopic grade solvents were used as received without further purification. 8-Hydroxyquinoline was purchased from Qualigen and Aluminium isopropoxide was purchased from Aldrich chemicals (USA). Melting points were determined in capillary tubes and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively, on a Bruker 500 MHz spectrometer. *J* values are given in Hz. Mass spectral data were obtained on a Thermo Finnigan LCQ-Deca series electro spray ion trap mass spectrometer (ESI-MS). Elemental analyses were performed in Theoquest C.E. Instruments EA1112. Thin films of complexes on glass substrate (1 cm^2) were made by spin coating from *o*-xylene solution and thickness was determined by redissolving the film in dichloromethane.

2.2. Spectroscopic measurements and techniques

The absorption and steady-state fluorescence spectra were recorded using Shimadzu UV2100 and Spex Fluorolog 1681 spectrophotometer, respectively. Fluorescence measurements of thin films were done for excitation/emission geometry of 22.5° instead of the usual 90° geometry for solutions in a cuvette. A concentration of (ca. 1 mM) stock solution was prepared separately for each complex by dissolving the required amount of the compound in respective solvents. The solutions for spectral measurements were prepared by adding the appropriate amount of the complex to maintain its concentration at 25–100 μM for all the complexes. The fluorescence measurements were done by excitation at the absorption maximum. Fluorescence quantum yields of the complexes were determined in dichloromethane, relative to AlQ_3 in dichloromethane, taking into account absorbance and area of the emission spectra. Fluorescence lifetime measurements were made using a TCSPC spectrometer [16] using picosecond laser pulses at high repetition rate (4 MHz). The fluorescence decay was fitted to a multi-exponential function by a standard method [16] and average lifetime was calculated using the equation $\tau_{avg} = (\tau_1\alpha_1 + \tau_2\alpha_2)/(\alpha_1 + \alpha_2)$.

2.3. Electroluminescence

The OLED was built as a sandwich device using patterned pre-cleaned indium-tin oxide (ITO) coated glass substrate (resistance 6 Ω, Delta Technologies, USA) as the transparent anode. PEDOT-PSS (poly(styrenesulfonate)/poly(2,3-dihydrothieno[3,4-*b*]-1,4-dioxin), Bayer, Germany) was spin-coated on ITO as a hole transport layer. Electroluminophore $Al(\mathbf{3})_3$ was spin-coated in the form of its *o*-xylene solution (3.5 mg/100 μl). Spin speed was maintained at 2700 rpm. Then LiF (10 Å) was deposited by thermal evaporation over the electroluminophore at a pressure of 10^{-7} Torr. Al was evaporated on top of LiF film which is the cathode. Typical device areas were 1.5 mm^2.

2.4. Synthesis of ligands, **2–9**

2.4.1. 5-Chloromethyl-8-hydroxyquinoline hydrochloride

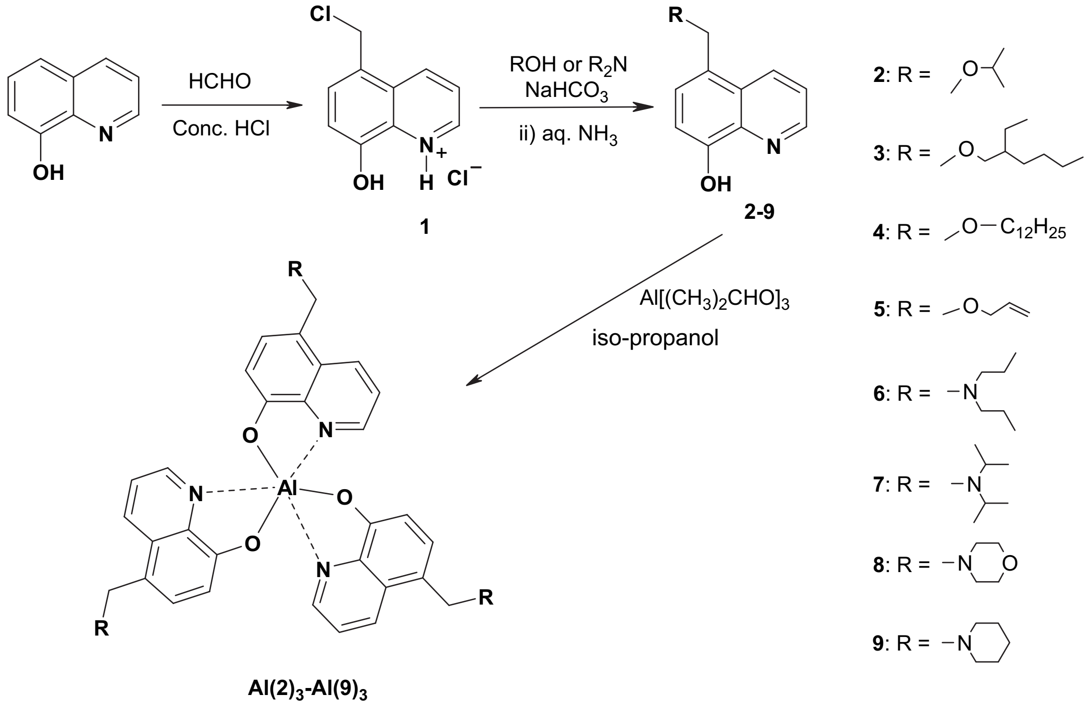
5-Chloromethyl-8-hydroxyquinoline hydrochloride (**1**) was synthesised according to the literature procedure [11].

2.4.2. 5-iso-Propyloxymethyl-8-hydroxyquinoline (**2**)

To a suspension of **1** (2 g, 8.7 mmol) in isopropanol (20 ml) was added sodium bicarbonate (0.73 g, 8.7 mmol). The reaction mixture was warmed in a water bath with occasional shaking until the solvent was evaporated. The yellow residue was dissolved in water and treated with dilute ammonia. The white solid formed was filtered and dried. Recrystallisation from

Table 1
Detail characterisation data for the ligands (**2–9**)

Compd	Mol. formula (mol. wt)	Yield (%)	M.P. (°C)	Calcd. (%). Found (%)	^{1}H NMR ($CDCl_3$) δ assignment	^{13}C NMR ($CDCl_3$) δ assignment	ESI-mass $(M+H)^+$
2	$C_{13}H_{15}NO_2$ (217.27)	90	65–67	C, 71.86; H, 6.96; N, 6.45. C, 71.53; H, 6.67; N, 6.46.	1.28 (d, 6H, CH_3), 3.78 (m, 1H, OC*H*), 4.87 (s, 2H, OCH_2), 7.13 (d, 1H, *J* 7.5 Hz), 7.46 (d, 1H, *J* 7.5 Hz), 7.53 (dd, 1H, *J* 4 Hz, *J* 4 Hz), 8.54 (d, 1H, *J* 8.5 Hz), 8.83 (d, 1H, *J* 4 Hz).	21.69 (CH_3), 68.22 (OCH), 70.71 (OCH_2), 108.8, 121.85, 125.02, 127.49, 128.55, 133.55, 138.76, 147.65, 152.34 (Ar)	218.13
3	$C_{18}H_{25}NO_2$ (287.41)	55	Liq.	C, 75.22; H, 8.77; N, 4.87. C, 75.11; H, 8.67; N, 4.77	0.86 (t, 6H, CH_3), 1.1-1.5 (m, 9H), 3.39 (d, 2H, OCH_2), 4.85 (s, 2H, CH_2Ar), 7.13 (d, 1H, *J* 7.5 Hz), 7.46 (d, 1H, *J* 7.5 Hz), 7.52 (dd, 1H, *J* 4 Hz, *J* 4 Hz), 8.55 (d, 1H, *J* 8.5 Hz), 8.83 (d, 1H, *J* 4.5 Hz)	14.15 (CH_3), 22.55, 26.03, 29.26 (CH_2), 70.1 (OCH_2), 70.71 (OCH_2), 108.8, 121.85, 125.02, 127.49, 128.55, 133.55, 138.76, 147.65, 152.34 (Ar).	288.3
4	$C_{22}H_{33}NO_2$ (343.51)	60	54–66	C, 76.92; H, 9.68; N, 4.08. C, 77.1; H, 9.71; N, 3.56.	0.92 (t, 3H, CH_3), 1.33 (br, 18H, CH_2), 1.63 (q, 2H, OCH_2CH_2), 3.52 (t, 2H, OCH_2), 4.86 (s, 2H, OCH_2), 7.13 (d, 1H, *J* 7.5 Hz), 7.45 (d, 1H, *J* 7.5 Hz), 7.53 (dd, 1H, *J* 4 Hz, *J* 4 Hz), 8.54 (d, 1H, *J* 8.5 Hz), 8.83 (d, 1H, *J* 4 Hz)	14.08 (CH_3), 22.61, 26.14, 29.34, 31.85 (CH_2), 70.06 (OCH_2), 70.85 (OCH_2), 108.8, 121.65, 124.65, 127.41, 128.51, 133.48, 138.62, 147.56, 152.39 (Ar).	344.4
5	$C_{13}H_{13}NO_2$ (215.25)		81–83	C, 72.54; H, 6.09; N, 6.51. C, 72.58; H, 6.18; N, 6.46.	4.08 (d, 2H, OCH_2, *J* 5.5 Hz), 4.9 (s, 2H, OCH_2), 5.26 (d, 1H, *cis*, *J* 10.5 Hz), 5.34 (d, 1H, *trans*, *J* 17 Hz), 5.99 (m, 1H, OCH_2CH), 7.14 (d, 1H, *J* 8 Hz), 7.46 (d, 1H, *J* 7.5 Hz), 7.54 (dd, 1H, *J* 4 Hz, *J* 4 Hz), 8.55 (d, 1H, *J* 8.5 Hz), 8.8 (d, 1H, *J* 4.5 Hz).	69.94, 70.59 (OCH_2), 108.82 (Ar), 117.38, 117.54 (allyl CH_2), 121.82, 124.26, 127.42, 128.77, 133.39 (Ar), 134.5 (allyl CH), 138.6, 147.63, 152.48 (Ar).	216.2
6	$C_{16}H_{22}N_2O$ (258.37)	75	82–84	C, 74.38; H, 8.58; N, 10.84. C, 74.51; H, 8.64; N, 10.78	0.84 (t, 6H, CH_3), 1.52 (m, 4H, CH_2), 2.43 (t, 4H, NCH_2), 3.9 (s, 2H, NCH_2), 7.11 (d, 1H, J 8 Hz), 7.4 (d, 1H, J 8 Hz), 7.47 (dd, 1H, J 4.5 Hz, J 4.5 Hz), 8.8 (dd, 2H, J 5 Hz, J 2.5 Hz).	11.86 (CH_3), 19.78 (NCH_2CH_2), 55.5 (NCH_2CH_2), 57.18 (NCH_2), 108.56, 121.05, 126.36, 127.8, 128.48, 134.21, 138.6, 147.36, 151.37 (Ar)	259
7	$C_{16}H_{22}N_2O$ (258.37)	55	131–133	C, 74.38; H, 8.58; N, 10.84. C, 74.44; H, 8.61; N, 10.72.	1.1 (d, 12H, CH_3), 3.09 (q, 2H, NCH), 4.05 (s, 2H, NCH_2), 7.12 (d, 1H, J 8 Hz), 7.45 (dd, 1H, J 4 Hz, J 4 Hz), 7.53 (d, 1H, J 7.5 Hz), 8.8 (d, 1H, J 3.5 Hz), 8.85 (d, 1H, J 8.5 Hz).	20.86 (CH_3), 39.23 (NCH), 39.78 (NCH_2), 108.26, 121.15, 126.43, 127.79, 128.45, 134.21, 138.61, 147.38, 151.27 (Ar)	259
8	$C_{14}H_{16}N_2O_2$ (244.3)	72	134–136	C, 68.83; H, 6.6; N, 11.47. C, 68.66; H, 6.41; N, 11.36.	2.5 (t, 4H, OCH_2), 3.7 (t, 4H, NCH_2), 3.84 (s, 2H, NCH_2), 7.11 (d, 1H, J 7.5 Hz), 7.38 (d, 1H, J 7.5 Hz), 7.52 (dd, 1H, J 4 Hz, J 3.5 Hz), 8.72 (d, 2H, J 8.5 Hz), 8.83 (d, 1H, J 3 Hz).	53.3 (OCH_2), 61.1 (NCH_2), 67.1 (OCH_2), 108.59, 121.43, 124.06, 127.86, 129.04, 134.04, 138.7, 147.56, 151.89 (Ar).	245
9	$C_{15}H_{18}N_2O$ (242.32)	45	97–99	C, 74.35; H, 7.49; N, 11.56. C, 74.5; H, 7.41; N, 11.42	1.47 (q, 2H, CH_2), 1.56 (q, 4H, NCH_2CH_2), 2.43 (bs, 4H, NCH_2), 3.79 (s, 2H, NCH_2), 7.11 (d, 1H, J 7.5 Hz), 7.36 (d, 1H, J 7.5 Hz), 7.5 (dd, 1H, J 4 Hz, J 3.5 Hz), 8.75 (d, 2H, J 8.5 Hz), 8.81 (d, 1H, J 3 Hz).	22.58 ($NCH_2CH_2CH_2$), 27.26 (NCH_2CH_2) 57.78 (NCH_2), 67.26 (NCH_2), 108.59, 121.43, 124.06, 127.86, 129.04, 134.04, 138.7, 147.56, 151.89 (Ar).	243.2



Scheme 1. Synthetic route of 5-substituted 8-hydroxyquinoline ligands (**2**–**9**) and their Al(III) complexes Al(**2**)$_3$–Al(**9**)$_3$.

petroleum ether afforded 1.7 g of **2** as a white needle shape crystalline solid. Detailed characterisation data are given in Table 1.

5-(2-Ethylhexyloxymethyl)-8-hydroxyquinoline (**3**), 5-dodecyloxymethyl-8-hydroxyquinoline (**4**), 5-alyloxymethyl-8-hyroxyquinoline (**5**) were synthesised following a similar procedure as **2** and given in detail in Table 1.

2.4.3. 5-Di-propylaminomethyl-8-hydroxyquinoline (6)

To a suspension of **1** (2 g, 8.7 mmol) in ethylacetate was added dipropylamine (3 time excess). The reaction mixture was warmed in a water bath with occasional shaking for 1 h. The white precipitate was filtered and washed with ethylacetate. The filtrate was evaporated to dryness and the residue was recrystallised from petroleum ether to give 1.68 g of **6** as white solid.

5-Di-isopropylaminomethyl-8-hydroxyquinoline (**7**), 5-morpholinomethyl-8-hydroxyquinoline (**8**), 5-piperidinomethyl-8-hydroxyquinoline (**9**) were synthesised following a similar procedure as for **6**. Detailed characterisation data are given in Table 1.

2.5. Synthesis of aluminium complex, Al(2)$_3$–Al(9)$_3$

2.5.1. General procedure for synthesis of complex Al(2)$_3$

To a solution of ligand **2** (500 mg, 2.3 mmol) in isopropanol (20 ml) was added aluminium isopropoxide (157 mg, 0.77 mmol). The resulting mixture was refluxed for 4–5 h. Then after cooling, the solvent was removed under vacuum and the yellow precipitate obtained was recrystallised from methanol/water mixture.

All other complexes Al(**3**)$_3$–Al(**9**)$_3$ were prepared following the above general procedure for Al(**2**)$_3$. Detailed characterisation data for all the complexes are given in Table 2.

3. Results and discussion

3.1. Synthesis

The ligands were designed to enhance the solubility of AlQ$_3$ without affecting the beneficial spectroscopic and luminescence properties. The solubility is enhanced by attaching side chains of alkoxy and alkylamine groups to the ligand. The ligands reported here have alkyl chains attached at the 5 position through an $-CH_2O-$ or $-CH_2N-$ as the bridge group. The $-CH_2-$ spacer group ensures minimal effect on the aromaticity of the ligand, irrespective of the alkyl group.

8-Hydroxyquinoline was reacted with formaldehyde and conc. HCl to afford **1** as its hydrochloride salt [11]. The reaction of **1** with corresponding alcohols and amines gives 5-substituted products **2**–**9** (Scheme 1). The structures of the ligands were confirmed by their ^{1}H and ^{13}C NMR, mass and elemental analysis. Reaction of the ligands with aluminium isopropoxide in isopropanol

Table 2
Detail characterisation data for the complexes (Al(**2**)$_3$–Al(**9**)$_3$)

Compd	Mol. formula (mol. wt)	Yield (%)	M.P. (°C)	^{1}H NMR 25 °C (DMSO-d$_6$) δ assignment	^{1}H NMR 125 °C (DMSO-d$_6$) δ assignment	ESI-Mass
Al(**2**)$_3$	$\mathrm{C_{39}H_{42}N_3O_6Al}$ (675.77)	95	162–164	1.12, 1.15 (d, $\mathrm{C}H_3$, *J* 7.5 Hz), 3.33, 3.72 (m, $\mathrm{OC}H$), 4.7, 4.78 (br, s, $\mathrm{OC}H_2$), 6.68, 6.84, 7.2, 7.4, 7.51, 7.55, 7.65, 7.74, 8.5-8.73 (br, Ar*H*)	1.2 (d, 18H, $\mathrm{C}H_3$, *J* 5 Hz), 3.8 (q, 3H, $\mathrm{OC}H$), 4.8 (s, 6H, $\mathrm{OC}H_2$), 6.85 (d, 1H, ArH, *J* 7.5 Hz), 7.5 (d, 1H, ArH, *J* 8 Hz), 7.6, 8,3 (br, 2H, ArH), 8.68 (d, 1H, ArH, *J* 8 Hz)	698.3 (M + Na)$^+$, 676.2 (M$^+$)
Al(**3**)$_3$	$\mathrm{C_{54}H_{72}N_3O_6Al}$ (886.17)	90	148–150	0.5-0.95 (br, $\mathrm{C}H_3$), 0.95-1.6 (br, $\mathrm{C}H_2$), 3.35 4.5-4.9 (br, $\mathrm{OC}H_2$), 6.71, 6.8-6.9, 7.4, 7.52, 7.63, 7.72, 8.5-8.9 (br, Ar*H*)	0.8 (t, 9H, $\mathrm{C}H_3$), 1.2-1.5 (br, m, 24H, $\mathrm{C}H_2$, C*H*), 1.6 (m, 3H, $\mathrm{C}H_2$), 3.45 (d, 6H, d, $\mathrm{OC}H_2$, *J* 5 Hz), 4.8 (s, 6H, $\mathrm{OC}H_2$), 6.85 (d, 1H, ArH, *J* 7.5 Hz), 7.5 (d, 1H, ArH, *J* 7.5 Hz), 7.65, 8.3 (br, 2H, ArH), 8.65 (d, 1H, ArH, *J* 8 Hz)	908.5 (M + Na)$^+$, 886.3 (M$^+$)
Al(**4**)$_3$	$\mathrm{C_{66}H_{96}N_3O_6Al}$ (1054.5)	90	145–147	0.88 (br, $\mathrm{C}H_3$), 1.0-1.6 (br, $\mathrm{C}H_2$), 3.5 (br, $\mathrm{OC}H_2$), 4.6-4.8 (m, $\mathrm{OC}H_2$), 6.69, 6.82, 7.38, 7.49, 7.62, 7.71, 8.55-8.7, 8.78 (br, Ar*H*)	0.7 (br, 3H, $\mathrm{C}H_3$), 0.88 (t, 6H, $\mathrm{C}H_3$), 1.1-1.4 (br, 60H, $\mathrm{C}H_2$), 1.65 (t, 6*H*, $\mathrm{C}H_3$), 3.55 (t, 6*H*, $\mathrm{OC}H_2$), 4.2-4.4 (s, 6H, $\mathrm{OC}H_2$), 6.78 (d, 1H, ArH, *J* 7 Hz), 7.41 (d, 1H, ArH, *J* 7.5 Hz), 7.6, 8.3 (br, 2H, ArH), 8.6 (d, 1H, ArH, *J* 8 Hz)	1076.7 (M + Na)$^+$, 1054.4 (M$^+$)
Al(**5**)$_3$	$\mathrm{C_{39}H_{36}N_3O_6Al}$ (669.62)	90	120–122	3.9-4.1 (br, $\mathrm{OC}H_2\mathrm{CH}$), 4.7-4.85 (m, $\mathrm{OC}H_2$), 5.14 (d, *cis H*, *J* 10 Hz), 5.25 (d, *trans H*, *J* 17 Hz), 5.95 (br, m, $\mathrm{OCH_2C}H$), 6.7, 6.88, 7.02, 7.4, 7.5, 7.65, 7.73, 8.5, 8.6-8.78, 8.81 (br, Ar*H*)	4.1 (d, 6H, $\mathrm{OC}H_2\mathrm{CH}$), 4.8 (s, 6H, $\mathrm{OC}H_2$), 5.15 (d, 1H, *cis H*, *J* 10 Hz), 5.31 (d, 1H, *trans H*, *J* 17 Hz), 6.0 (br, m, 3H, $\mathrm{OCH_2C}H$), 6.8 (d, 1H, ArH, *J* 7.5 Hz), 7.5 (d, 1H, ArH, *J*8 Hz), 7.65, 8.3, (br, 2H, ArH), 8.7 (d, 1H, ArH, *J* 8 Hz)	692.3 (M + Na)$^+$, 670.1 (M)$^+$
Al(**6**)$_3$	$\mathrm{C_{48}H_{63}N_6O_3Al}$ (799.06)	93	185–187	0.5-0.9 (br, $\mathrm{C}H_3$), 1.25-1.6 (br, $\mathrm{CH_3C}H_2$), 2.2-2.45 (br, $\mathrm{NC}H_2$), 3.75-3.95 (br, $\mathrm{NC}H_2$), 6.7, 6.84, 7.3, 7.4, 7.45, 7.6, 7.71, 8.65, 8.7-8.9 (br, Ar*H*)	0.8 (t, 18H, $\mathrm{C}H_3$), 1.45 (m, 12H, $\mathrm{CH_3C}H_2$), 2.4 (t, 12H, $\mathrm{CH_2C}H_2\mathrm{N}$), 3.9 (s, 6H, $\mathrm{NC}H_2$), 6.8 (d, 1H, ArH, *J* 7.5 Hz), 7.45 (d, 1H, ArH, *J* 7.5 Hz), 7.54, 8.25, (br, 2H, ArH), 8.82 (d, 1H, ArH, *J* 8 Hz)	822.1 (M + Na)$^+$, 799.1 (M$^+$)
Al(**7**)$_3$	$\mathrm{C_{48}H_{63}N_6O_3Al}$ (799.06)	75	> 275	0.6-1.2 (br, $\mathrm{C}H_3$), 3.1 (br, C*H*), 4.5-4.9 (br, $\mathrm{NC}H_2$), 6.5-7, 7.1-7.8, 8.1-9.1 (br, Ar*H*)	0.95, 1.05, 1.1 (3 × d, $\mathrm{C}H_3$), 3.05, 3.3 (m, C*H*), 4.01, 4.5-4.7 (m, $\mathrm{NC}H_2$), 6.7, 6.9, 7.35, 7.45, 7.5, 8.2-8.8 (br, ArH)	821.95 (M + Na)$^+$, 799.1 (M$^+$)
Al(**8**)$_3$	$\mathrm{C_{42}H_{45}N_6O_6Al}$ (756.85)	80	> 220 (d)[a]	1.3-1.6 (br, $\mathrm{NC}H_2\mathrm{CH_2}$), 2.45 (br, $\mathrm{OC}H_2$), 3.6-3.8 (br, $\mathrm{NC}H_2$), 6.65, 6.84, 7.37, 7.5, 7.64, 7.73, 8.65, 8.85 (br, Ar*H*)	1.4, 1.5 (br, 12H, $\mathrm{NC}H_2\mathrm{CH_2}$), 2.45 (br, 12*H*, $\mathrm{OC}H_2$), 3.75 (s, 6H, $\mathrm{NC}H_2$), 6.72 (d, 1H, ArH, *J* 7.5 Hz), 7.4 (d, 1H, Ar*H*, *J* 7.5 Hz), 7.5, 8.25, (br, 2H, ArH), 8.8 (d, 1H, ArH, *J* 8 Hz)	779.5 (M + Na)$^+$, 757.2 (M$^+$)
Al(**9**)$_3$	$\mathrm{C_{45}H_{51}N_6O_3Al}$ (750.93)	85	210–215	2.4 (br, $\mathrm{C}H_2$), 3.5, 3.65, 3.75 (br, $\mathrm{C}H_2$), 6.65, 6.82, 7.4, 7.5, 7.63, 7.73, 8.65, 8.85 (br, Ar*H*)	2.45 (br, 18H, $\mathrm{C}H_2$), 3.4-3.7 (br, 12H, $\mathrm{C}H_2$), 3.8 (s, 6H, $\mathrm{NC}H_2$), 6.75 (d, 1H, ArH, *J* 7.5 Hz), 7.45 (d, 1H, ArH, *J* 7.5 Hz), 7.55, 8.25, (br, 2H, ArH), 8.8 (d, 1H, ArH, *J* 8 Hz)	774.4 (M + Na)$^+$, 751.3 (M$^+$)

[a] d, decompose.

afforded the metal complexes Al(**2**)$_3$–Al(**9**)$_3$ as yellow solid. The octahedral aluminium complexes in principle exist in two different isomeric forms, *mer* (meridianal) and *fac* (facial), evidence for which can be recognisable from their ^{1}H NMR spectra [12]. The spectrum for each complex has three separate sets of ligand resonances at 25 °C, which indicates that the three ligands are situated around the metal ion such that each ligand is magnetically distinct [13]. ^{1}H NMR spectra of the aluminium complexes Al(**2**)$_3$–Al(**9**)$_3$ in DMSO-d_6 at room temperature indicated the presence of pure *mer* isomers, which is similar to the result previously reported for parent AlQ$_3$ [14a,b]. Interestingly, when these complexes in DMSO-d_6 are heated to 125 °C, ^{1}H NMR spectra collapse to a single set of ligand resonances, clearly indicating rapid interconversion between the ligands (details given in Section 2). Baker and Sawyer [13] have also observed that the spectral line of equivalent protons on different ligands collapsed to their average positions at 115 °C. Fig. 1 shows ^{1}H NMR spectra of Al(**2**)$_3$ and Al(**6**)$_3$ in DMSO at 25 °C and 125 °C and the proton peaks have been assigned. The mass spectral data of these complexes show peaks for M$^+$ and (M+Na)$^+$ further supports the assignment (see Table 2 for details).

3.2. Spectroscopic studies

AlQ$_3$ is soluble (~2 mM) only in dichloromethane (DCM). It is not possible to cast thin, glassy, transparent film of AlQ$_3$ from DCM because of rapid evaporation of DCM and/or crystallisation. The compounds Al(**2**)$_3$–Al(**9**)$_3$ are highly soluble in DCM as well as in many other organic solvents, approximately 25–100 times (~50 mM for Al(**7**)$_3$ and ~200 mM for Al(**3**)$_3$) more than that of AlQ$_3$. Thin, transparent film

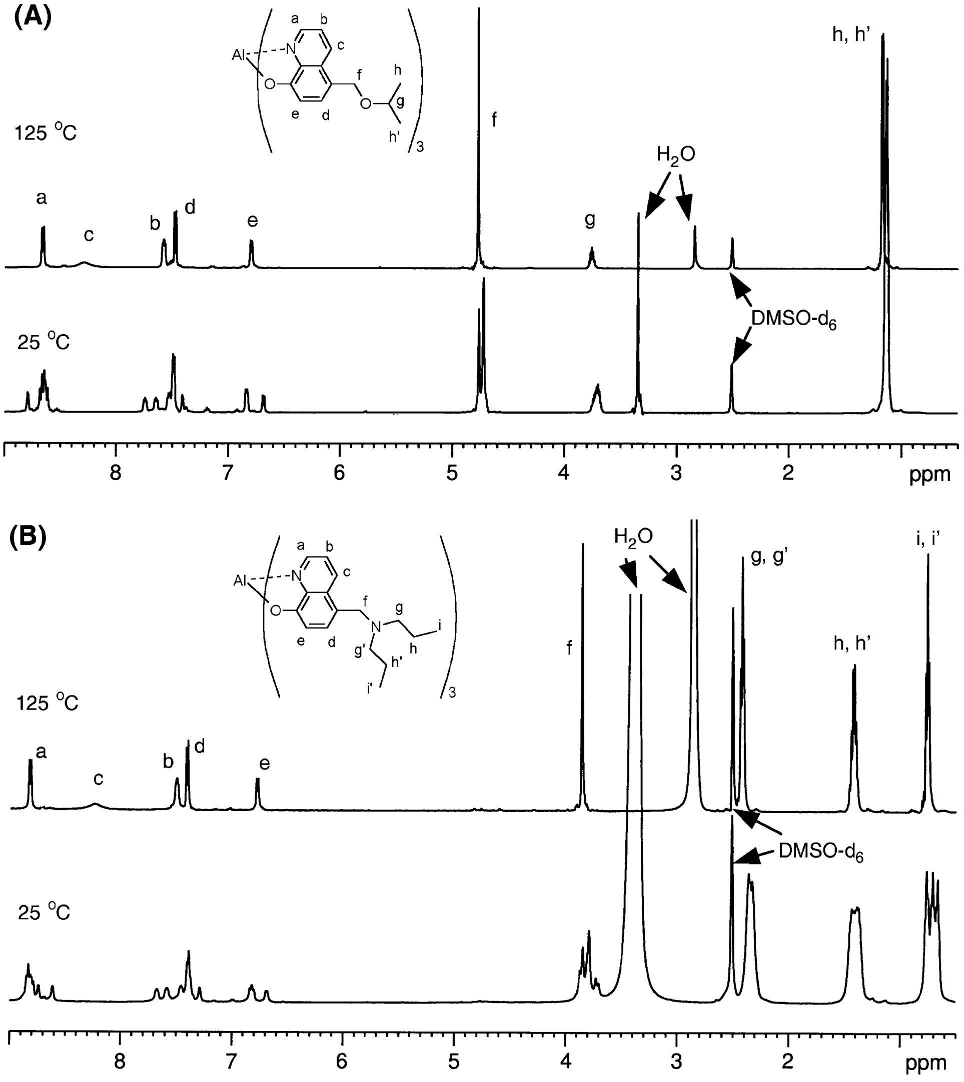


Fig. 1. Representative 500 MHz ^{1}H NMR spectrum of (A) Al(**2**)$_3$ and (B) Al(**6**)$_3$ in DMSO-d_6 at 25 °C and 125 °C. The spectrum collapses to a single ligand resonance at high temperature and all the protons were assigned.

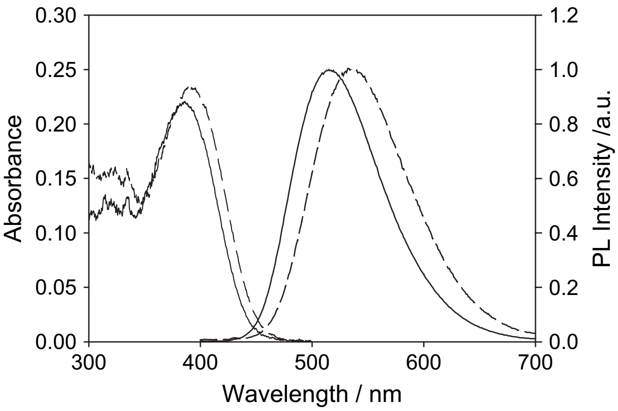


Fig. 2. Absorption and fluorescence emission spectrum of AlQ_3 (solid line) and complex Al(**3**)$_3$ (dashed line) in DCM solution.

Table 3
Spectroscopic data of complexes, AlQ_3 and complexes (Al(**2**)$_3$–Al(**9**)$_3$) measured DCM solution and in thin-film on glass substrate

Complexes	In solution		In thin-films		
	λ_{abs}/nm	λ_{em}/nm	ϕ_f[a]	λ_{abs}/nm	λ_{em}/nm
AlQ_3	384	516	1	370	527
Al(**2**)$_3$	391	536	0.35	395	531
Al(**3**)$_3$	392	536	0.38	400	527
Al(**4**)$_3$	391	536	0.39	399	536
Al(**5**)$_3$	390	533	0.37	397	535
Al(**6**)$_3$	395	536	0.32	402	531
Al(**7**)$_3$	395	540	0.36	400	529
Al(**8**)$_3$	393	532	0.45	396	530
Al(**9**)$_3$	392	527	0.46	399	528

[a] Absolute quantum yield of AlQ_3 in DCM is 0.22 [15].

of these complexes can be spin cast from the solution of *o*-xylene.

3.2.1. Absorption spectra in solution

The absorption spectra of Al(**2**)$_3$–Al(**9**)$_3$ were studied in DCM solution. The absorption spectra of the dyes were similar to AlQ_3, except for a slight bathochromic shift (Fig. 2). Table 3 shows the peaks of the absorption spectra, which includes the data for AlQ_3. These complexes have long wavelength absorption band in the range of 390–395 nm, which is assigned to the π–π^* transition. With respect to AlQ_3, these complexes show 6–11 nm bathochromic shift, as expected due to the presence of substituent (CH_2–X) at 5-position of 8-hydroxyquinoline. –CH_2– group is common to all the derivatives and hence the spectral shift is very small. Extinction coefficient ranges from 4600 to 9000 M^{-1} cm^{-1} for all the complexes.

3.2.2. Emission spectra in solution

The emission spectra of Al(**2**)$_3$–Al(**9**)$_3$ were also similar to AlQ_3, broad and highly Stokes shifted (Fig. 2). The peak of the emission spectrum of the complexes Al(**2**)$_3$–Al(**9**)$_3$ ranges from 527 to 540 nm in DCM. Similar to absorption, the emission spectra of all the complexes (Al(**2**)$_3$–Al(**9**)$_3$) are also red shifted with respect to AlQ_3 by 15–20 nm. The fluorescence quantum yields of Al(**2**)$_3$–Al(**9**)$_3$ were determined in DCM and the values are given in Table 3.

3.2.3. Fluorescence decay and lifetimes in solution

The fluorescence decays of the dyes were measured in DCM solution and compared with that of AlQ_3. The fluorescence decay of AlQ_3 is double exponential in DCM with a average lifetime of 16.72 ns [15]. The new complexes Al(**2**)$_3$–Al(**9**)$_3$ also show double exponential fluorescence decay in organic solvent (DCM). The complete lifetime data and amplitude of these complexes are shown in Table 4 and Fig. 3 shows the representative decay plot of Al(**3**)$_3$. It may be noted that the fluorescence quantum yield (Table 3) is approximately proportional to the fluorescence lifetime, which is to be expected if the nature of the emitting species is the same in all the solvents.

3.2.4. Spectra and lifetimes in thin films

Thin films of Al(**2**)$_3$–Al(**9**)$_3$ were spin-cast on glass substrate from the solution in *o*-xylene. The film thickness was estimated to be 50–60 nm. *o*-Xylene was found to be the best solvent for spin-casting purposes

Table 4
Fluorescence lifetime data of complexes Al(**2**)$_3$–Al(**9**)$_3$ in DCM and in thin-film

Complexes	In solution				In thin-films				
	τ_1/ns (α_1)	τ_2/ns (α_2)	τ_{avg}/ns	χ^2	τ_1/ns (α_1)	τ_2/ns (α_2)	τ_3/ns (α_3)	τ_{avg}/ns	χ^2
AlQ_3[a]	16.8 (0.99)	4.59 (0.01)	16.72	1.01	16.2 (0.62)	8.76 (0.11)	2.57 (0.12)	11.43	1.22
Al(**2**)$_3$	7.08 (0.39)	4.65 (0.61)	5.71	1.06	9.87 (0.70)	2.47 (0.30)	–	7.74	1.13
Al(**3**)$_3$	5.94 (0.72)	0.45 (0.28)	4.41	1.17	11.46 (0.75)	2.16 (0.25)	–	9.15	1.15
Al(**4**)$_3$	6.30 (0.79)	1.22 (0.21)	5.22	1.20	10.82 (0.73)	2.37 (0.27)	–	8.54	1.27
Al(**5**)$_3$	6.32 (0.93)	1.29 (0.07)	5.95	1.04	9.81 (0.75)	2.02 (0.25)	–	7.83	1.05
Al(**6**)$_3$	5.11 (0.74)	0.88 (0.26)	4.03	1.04	9.52 (0.65)	1.87 (0.35)	–	6.81	1.21
Al(**7**)$_3$	5.52 (0.58)	1.11 (0.42)	3.68	1.37	6.40 (0.19)	2.27 (0.38)	0.37 (0.43)	2.21	0.99
Al(**8**)$_3$	6.95 (0.76)	0.97 (0.24)	5.54	0.98	10.57 (0.65)	2.62 (0.35)	–	7.80	1.18
Al(**9**)$_3$	14.31 (0.24)	5.23 (0.76)	7.43	1.37	15.35 (0.12)	5.25 (0.38)	0.83 (0.50)	4.25	1.09

[a] Data taken from ref. [15].

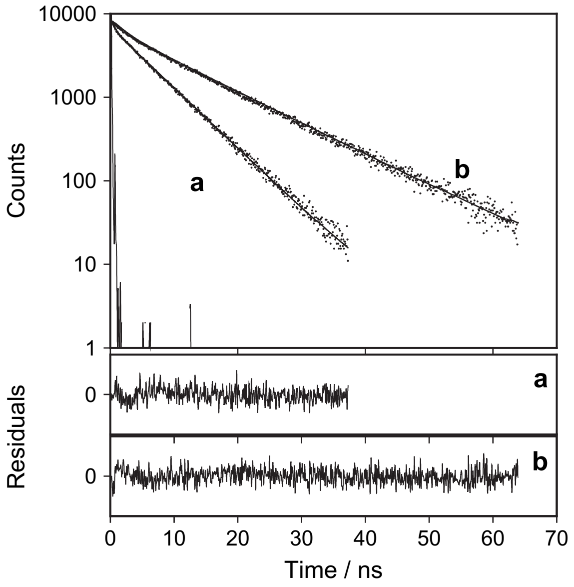


Fig. 3. Time resolved fluorescence decay of complex Al(**3**)$_3$ (a) in DCM, (b) in thin film on glass. The excitation function is also shown. Solid line represents the fitted data. The distribution of weighted residuals are shown in the bottom panels. The decay is fitted to a biexponential function ($\chi^2 = 1.15$) and the lifetimes are given in Table 4.

compared to other solvent. The films were dried, stored in a vacuum desiccator and were found to be indefinitely stable. All the films except Al(**4**)$_3$ and Al(**7**)$_3$ were glassy and transparent and spectral and lifetime measurements were measured. Figs. 3 and 4 show the lifetime decay and absorption/emission spectra of thin film of complex Al(**3**)$_3$, respectively. It may be noted that a comparable glassy film of AlQ$_3$ can be made only by vacuum deposition. The absorption and emission spectra of films of Al(**2**)$_3$–Al(**9**)$_3$ were similar to that of AlQ$_3$ film. The absorption peak of Al(**2**)$_3$–Al(**9**)$_3$ in thin film varies from 395 to 402 nm and the emission peak varies from 527 to 535 nm (Table 3). The luminescence quantum yield of Al(**2**)$_3$–Al(**9**)$_3$ in thin films could not be determined by a direct or relative method because of uncertain geometry constraint.

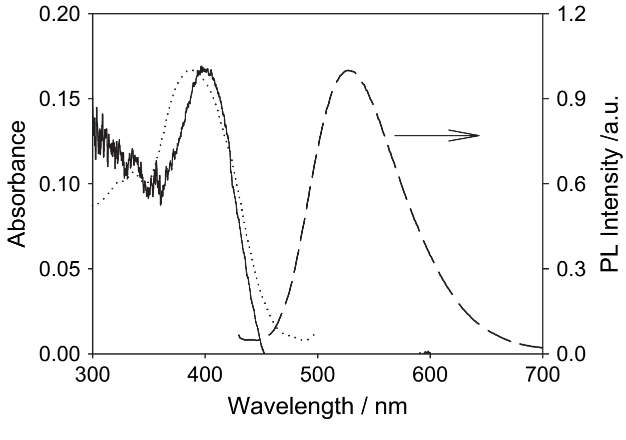


Fig. 4. Representative absorption spectrum of Al(**3**)$_3$ in thin film (solid line), emission spectrum (dashed line) and excitation spectrum (dotted line) on glass substrate.

The fluorescence decays of these dyes in thin films were measured. The decays were double or triple exponential and the measured values are shown in Table 4. The average lifetime for the decay in film is also shown in Table 4. It is significant to note that the average lifetime is maximum for Al(**3**)$_3$ which is less by only 20% compared to AlQ$_3$. The average lifetimes of other films except Al(**7**)$_3$ were also substantially high in thin films.

3.3. Electroluminescence

The motivation for synthesising these new complexes Al(**2**)$_3$–Al(**9**)$_3$ is their potential use in OLEDs, given the potential sensitivity of substituents to the electron injection. Simple OLED devices were fabricated using ITO-modified glass (anode), PEDOT-PSS (hole-transport layer), complex Al(**3**)$_3$ (electron-transport layer, spin-coated from *o*-xylene), LiF and Al (cathode). The advantage of using PEDOT-PSS polymer is to smoothen the anode surface and facilitated hole injection in the device and reduction of the probability for electrical shorts. The device fabricated using complex Al(**3**)$_3$ showed turn-on voltages for light emission at approximately 11 V (Fig. 5).

4. Conclusion

We have prepared some new 5-substituted 8-hydroxyquinoline derivatives and their metal complex dyes with Al(III). It was shown that these new dyes lend high solubility in most of the organic solvents as compared to AlQ$_3$. As the substitution at 5-position of 8-hydroxyquinoline was aimed at obtaining good solubility, the

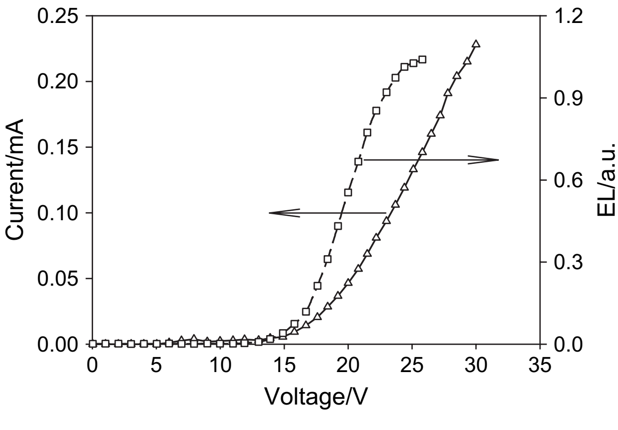


Fig. 5. A plot of electrical characteristic of an ITO/PEDOT-PSS/Al(**3**)$_3$/LiF/Al device. Solid line represents the current-voltage characteristics and dashed line represents the electroluminescent light intensity vs voltage (V).

results were encouraging and the complexes formed stable solution in *o*-xylene. These derivatives can easily be spin-coated on glass and other substrates of desirable thickness for thin film applications. These materials emit in the range of 527–536 nm, with a quantum yield of 2–3 times less as compared to AlQ_3. Although fluorescence quantum yield of some of these derivatives is slightly less than AlQ_3, the improved solubility of these compounds in organic solvents and formation of good quality transparent films make them useful for practical application in organic light emitting devices. The EL of device made by spin-cast film of $Al(\mathbf{3})_3$ shows the advantage of these organic soluble complexes in future application for OLEDs.

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