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Absorption and photoluminescence properties of 4-substituted Alq_3 derivatives and tris-(4-hydroxypyridinoanthrene)aluminum

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ABSTRACT

A series of 4-substituted Alq_3 derivatives have been synthesized. Photophysical properties of the complexes in solution have been studied in detail. The results show that Hammett σ_p constants of the substituents have a linear correlation with the emission maximum values of the aluminum complexes. Substitution at the 4-position improves the color purity of the emission and it has also a strong influence on the quantum yields. A new type of Alq_3 derivative, tris-(4-hydroxypyridinoanthrene)aluminum, has a good quantum yield and high emission color purity.

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1. Introduction

Since Tang and VanSlyke reported the first efficient organic light-emitting diode (OLED) in which tris-(8-hydroxyquinoline)-aluminum (Alq_3) formed the combined electron transport and emission layer, the parent Alq_3 has been widely used as a green emitter material in OLED devices (e.g., flat-panel displays) because of its good photophysical properties such as the high quantum yield.[1] Considerable recent interest has been focused on tuning of the emission properties by chemical modification of the 8-hydroxyquinoline ligand of the parent Alq_3. The emission properties are determined by electronic π–π^* transitions in the organic ligands. The π–π^* transitions can, in turn, be modified by adding suitable substituents to different positions of the quinoline ring. Steric factors favor positions 4 and 5[2] and, for example, a methyl substituent at the 2-position makes the aluminum tris-chelate unstable.[3] Substitution of the 5-position has been researched thoroughly[4] but only a few studies have been dedicated to positions 3, 4, 6, and 7.[4b,f,5]

Theoretical molecular orbital studies have shown that HOMOs are localized mainly on the positions 5 and 7 at the phenoxide part of the ligand while LUMOs mainly localize on the positions 2 and 4 at the pyridyl part of the ligand.[2,6] Thus, an electron donating group (EDG) at the 4-position should raise the LUMO energy levels and an electron withdrawing group (EWG) at the 5-position should lower the HOMO energy levels. As a result of these substitution strategies, the HOMO–LUMO gap is expected to increase.[2]

In this paper, the synthesis of 4-substituted Alq_3 derivatives is reported. The photophysical properties of the complexes are studied in detail. The results show that Hammett σ_p constant values of the substituents can be used to predict some of these properties.

2. Results and discussion

2.1. Syntheses and characterization

New Alq_3 derivatives **2a**–**o** have been synthesized from aluminum isopropoxide (method A) or aluminum nitrate (method B) and 4-substituted 8-hydroxyquinoline ligands **1a**–**n** (Scheme 1) and 4-hydroxypyridinoanthrene **1o**. The ligands were synthesized as reported previously.[7] The parent Alq_3 was bought from a commercial source. The products have been characterized with ^{1}H NMR and HRMS measurements. The parent Alq_3 as an octahedral complex can exists in the meridianal and facial isomer forms (Fig. 1) of which only the meridianal isomer is present in solution at room temperature.[8] ^{1}H NMR spectrum of the meridianal isomer of the parent Alq_3 shows two H2 signals at low field.[8,9] Similarly, two H2 signals can be observed from the ^{1}H NMR spectra of the 4-substituted Alq_3 derivatives thus they exist as pure meridianal isomers.

^{1}H NMR spectra were measured with Bruker Avance DPX200 instrument and high resolution mass spectra with Micromass LCT mass spectrometer. Absorption spectra were measured with Shimadzu UV-1601 UV–visible spectrophotometer and PL spectra with Jobin Yvon–Spex Fluoromax-2 spectrofluorometer. Samples used in absorption and fluorescence measurements were prepared by dissolving a certain amount of the aluminum complex in aerated $CHCl_3$. Sample concentrations were 20 μM. Photophysical data of the complexes are presented in Table 1.

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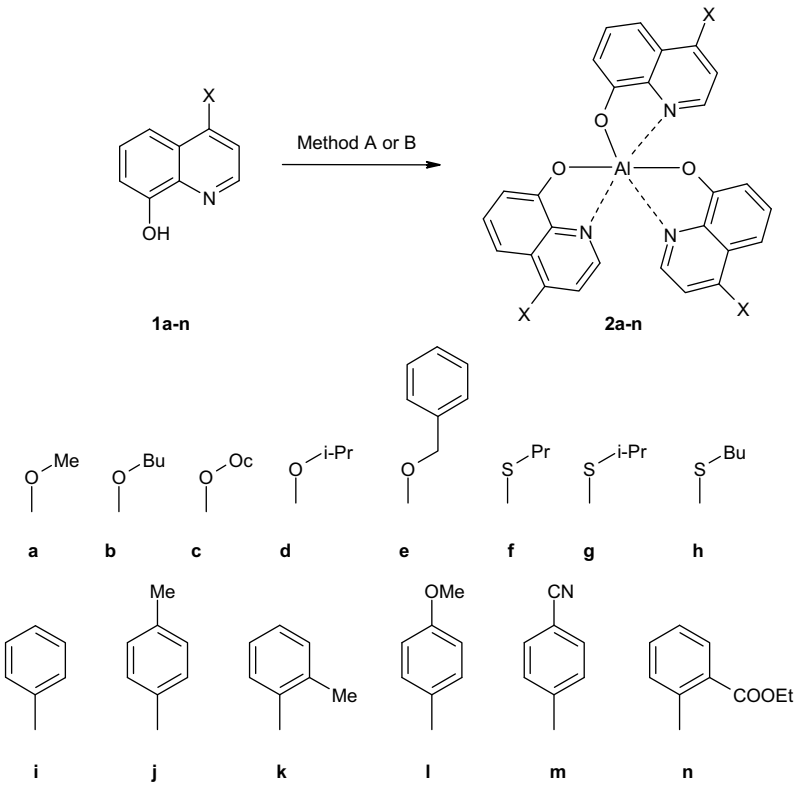

Scheme 1.

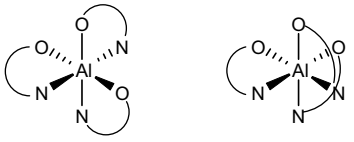

Figure 1. Meridianal and facial isomer forms of the parent Alq_3.

2.2. Absorption properties of the complexes

UV–vis absorption spectra show that aryl substituents shift absorption maxima of the complexes **2i**–**n** 4–25 nm to longer wavelength compared with the parent Alq_3 (Table 1, entries 1 and 10–15). This bathochromic effect is doubtless a consequence of extended conjugation caused by the phenyl ring.[10] Apparently, conjugation is much more effective when the π orbital systems of the aromatic substituent and the quinoline ring interact with each other compared with a situation where the π orbital system of the quinoline ring interacts with lone pair carrying orbitals of the substituent at the 4-position. In addition to the aromatic substituent in **2m** (entry 14), the cyano group also lengthens the conjugation further. A methyl substituent at the *ortho*-position of the aromatic substituent causes steric hindrance and restricts twisting around the phenyl–quinoline single bond.[10a] This means that a high π orbital conjugation in the excited state is energetically less favorable in the *ortho*-substituted compound **2k** (entry 12) than it is in the *para*-substituted compound **2j** (entry 11) and as a consequence an *ortho*-substituent on the phenyl ring decreases the bathochromic effect. This explains also the relatively small bathochromic effect of compound **2n** (entry 15).

Absorption maxima of compounds **2f**–**h** (entries 7–9) are situated in the same area compared with the absorption maximum of the parent Alq_3 (entry 1). It seems that the lone pair orbitals of thioalkyl substituents at the 4-position do not change the length of conjugation system of quinoline ligands. On the other hand, the alkoxy substituents in compounds **2a**–**e** (entries 2–6) shorten the wavelength of absorption considerably. This observation is even more interesting when these results are compared with the results of computer simulations presented by Curioni and Andreoni.[2] The calculations predict that the absorption maximum of tris-(4-hydroxy-5-(1,2,2-trifluoroethenyl)-8-hydroxyquinoline)-aluminum is blue-shifted to about 375 nm from 400 nm for the parent Alq_3. Results of our present study show clearly that an alkoxy substituent at the 4-position is powerful enough to alter the π–π^* system strongly and increase the optical band gap notably.

Table 1 shows also clearly that Alq_3 derivatives equipped with substituents, which donate electrons strongly, e.g., have moderately negative Hammett σ_p values have high optical band gaps and Alq_3 derivatives equipped with electron withdrawing substituents e.g., substituents with slightly positive Hammett σ_p values have lower optical band gaps compared with the parent Alq_3.

2.3. Photoluminescence properties of the Alq_3 derivatives

Strong EWGs, a piperidinylsulfonamide group (σ_p=+0.51)[12] and a 4,6-dimethoxy-1,3,5-triazinyl group at the 5-position of the 8-hydroxyquinoline ligand have previously been observed to cause the most substantial blue-shifts (34 nm and 36 nm, respectively).[4a,g] It has also been reported that a methyl group (σ_p=−0.17) at the 4-position of the 8-hydroxyquinoline ligand causes a 19 nm blue-shift compared with the parent Alq_3.[4b] Photoluminescence spectra of our compounds show that alkoxy substituents at the 4-position of the 8-hydroxyquinoline ligand cause the largest blue-shifts of 42–47 nm so far among Alq_3 derivatives (Fig. 2 and Table 1, entries 2–6). It seems that addition of strong EDGs to the 4-position

Table 1
Absorption and photoluminescence data of Alq_3 derivatives

Entry	Compound	Substituent	λ_{abs}[a] [nm], (ε)	λ_{PL}[b] [nm]	Φ[c]	Stokes' shift [cm^{-1}]	E_{gap}[d] [eV]	σ_p[e] (Ref.)	CIE (x, y), hue (purity)[f]
1	Alq_3	H	390 (6.5×10^3)	511	1.00	6100	3.18	0	(0.26, 0.51), green (42%)
2	**2a**	MeO	363 (1.2×10^4)	466	0.84	6100	3.42	−0.29 (11a)	(0.16, 0.21), blue (67%)
3	**2b**	BuO	363 (7.8×10^3)	467	1.36	6150	3.42	−0.32 (11b and c)	(0.16, 0.22), blue (65%)
4	**2c**	OcO	363 (1.3×10^4)	464	1.20	6010	3.42	−0.34 (11b, for pentyloxy)	(0.16, 0.20), blue (67%)
5	**2d**	*i*-PrO	362 (1.2×10^4)	469	1.04	6330	3.43	−0.45 (11b and c)	(0.16, 0.22), blue (65%)
6	**2e**	BzO	365 (1.3×10^4)	465	0.66	5920	3.40	−0.42 (11c)	(0.16, 0.20), blue (69%)
7	**2f**	*n*-PrS	391 (1.4×10^4)	540	0.53	7060	3.17	0.05 (12)	(0.37, 0.56), yellowish green (81%)
8	**2g**	*i*-PrS	393 (1.4×10^4)	544	0.47	7090	3.16	0.07 (11b)	(0.38, 0.56), yellow-green (86%)
9	**2h**	*n*-BuS	388 (1.4×10^4)	537	0.57	7150	3.20	0.05 (12)	(0.33, 0.50), yellowish green (54%)
10	**2i**	Ph	402 (9.3×10^3)	540	0.77	6370	3.09	−0.01 (11b and c)	(0.37, 0.56), yellowish green (83%)
11	**2j**	*p*-MePh	403 (1.0×10^4)	537	0.95	6220	3.08	−0.03 (11c)	(0.36, 0.56), yellowish green (80%)
12	**2k**	*o*-MePh	394 (8.9×10^3)	524	1.52	6300	3.15	0.01 (12)	(0.31, 0.54), yellowish green (62%)
13	**2l**	*p*-MeOPh	402 (1.2×10^4)	530	1.25	6030	3.09	−0.08 (11b)	(0.34, 0.56), yellowish green (74%)
14	**2m**	*p*-CNPh	415 (9.5×10^3)	579	0.04	6830	2.99	0.21 (12)	(0.48, 0.48), yellow (90%)
15	**2n**	*o*-COOEtPh	398 (8.0×10^3)	544	0.27	6770	3.12	0.10 (12, for methylester)	(0.40, 0.55), yellow-green (86%)
16	**2o**	Tetracyclic	469 (3.2×10^4)	538	1.21	2730	2.64	—	(0.41, 0.56), yellow-green (92%)

[a] Absorption maximum and the molar extinction coefficient.
[b] Photoluminescence maximum.
[c] Relative photoluminescence quantum yield.[13]
[d] Optical band gap ($E=hc/\lambda_{abs}$).[4a]
[e] Hammett σ_p constant.
[f] CIE chromaticity coordinates and color purity.[14]

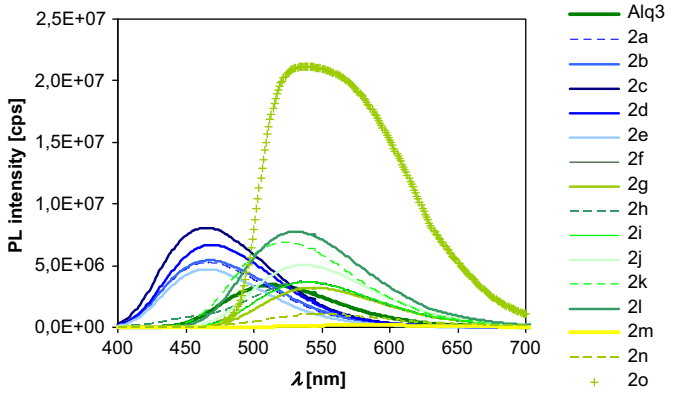

Figure 2. Photoluminescence spectra of aluminum complexes. Absorption maxima have been used as excitation wavelengths.

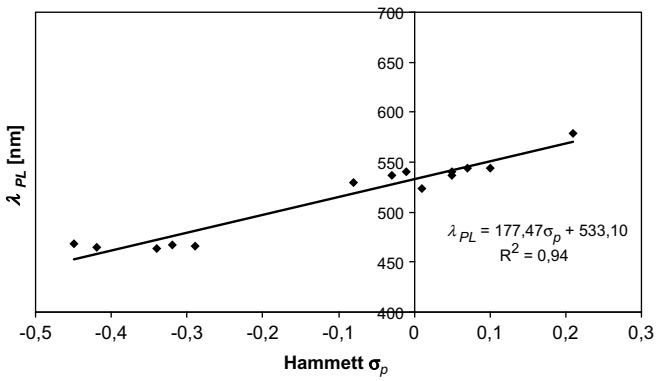

Figure 3. The correlation between photoluminescence maximum values of the 4-substituted Alq_3 derivatives and Hammett σ_p constants of the substituents.

of the 8-hydroxyquinoline ligand results in larger blue-shifts than the addition of strong EWGs to the 5-position of the 8-hydroxyquinoline ligand. On the other hand, both substitution positions seem to produce equally effective red-shifts. It has been observed that relatively weak EDGs such as a *p*-methoxyphenyl group or a methyl group at the 5-position of the 8-hydroxyquinoline ligand cause 38 nm and 33 nm red-shifts, respectively.[4a,g] Our present results show that weak electron withdrawing thioalkyl groups at the 4-position produce 26–33 nm red-shifts (entries 7–9) and that aryl substituents at the 4-position of the 8-hydroxyquinoline ligand produce 13–68 nm red-shifts of the PL emission (entries 10–15). It has previously been observed in the literature that Hammett σ_p correlate both with fluorescence lifetime and quantum yield in a relatively narrow homological series of 5-substituted Alq_3 derivatives.[4g] Our studies show that Hammett σ_p correlate well with λ_{PL} (Fig. 3) although the chemical nature and structure of the substituents vary considerably. The Hammett σ_p constant can clearly be used as a tool to predict the emission maximum of Alq_3 derivatives.

2.4. Stokes' shifts

The same magnitude of Stokes' shifts, in other words the energy losses between excitation and emission, in alkoxy substituted Alq_3 derivatives **2a–c** and the parent Alq_3 indicate that the geometry of these compounds varies similarly between the ground state and the excited state (entries 1–4).[15] The sterically more hindered isopropoxy group has larger barriers[16] between different conformations, which result in a larger Stokes' shift compared with Stokes' shifts of other alkoxy substituents (entries 2–6). All aryl substituents increase the Stokes' shift compared with the parent Alq_3 and it seems that both extended conjugation (entries 14 and 15) and *ortho*-substitution (entries 12 and 15) increase the Stokes' shifts. *ortho*-Substitution is likely to raise the steric barrier between ground state and excited states conformations, which lead to an increase in Stokes' shifts.[10a,15] A final observation is that thioalkyl substituted complexes **2f–h** have considerably larger Stokes's shifts compared with alkoxy analogues (entries 3, 5, and 7–9). A reasonable explanation is that thioalkyl substituents increase the

solvent relaxation effect because sulfur has a higher effective atomic polarizability than oxygen.[17] The increase in polarity of fluorophore increases the sensitivity of the excited state to solvent relaxation and a larger Stokes' shift occurs.[17b]

2.5. Photoluminescence quantum yield

In contrast to the previous observations that 5-substituted Alq_3 derivatives have a positive linear correlation between quantum yields and Hammett σ_p constants of the substituents,[4g] the PL quantum yields of aryl and thioalkyl substituted Alq_3 derivatives (entries 7–11 and 13–15) seem to have a negative linear correlation with Hammett σ_p constants (Fig. 4). On the other hand, quantum yields of the alkoxy derivatives and compound **2k** do not show good correlation with the Hammett σ_p constants. The presence of a branched isopropyl group decreases the quantum yield both in alkoxy and in thioalkyl series compared with corresponding Alq_3 derivatives with linear alkyl chains (entries 3–5 and 7–9). In the alkoxy series, the methoxy and benzyloxy groups (entries 2 and 6) seem to enhance the non-radiative decay from the excited state.

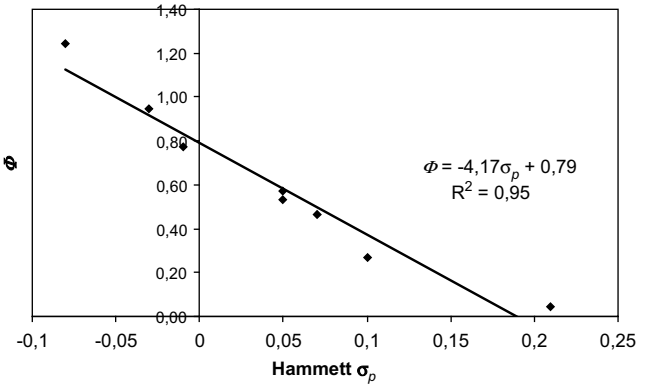

Figure 4. The correlation between quantum yields of the aryl and the thioalkyl substituted Alq_3 derivatives and Hammett σ_p constants of the substituents.

2.6. The emission colors of the Alq_3 derivatives

The emission colors from the Alq_3 derivatives are presented in Table 1 as their CIE 1931 chromaticity coordinates. The parent Alq_3 has a green hue of emission while aryl substituted complexes **2i**–**l** (entries 10–13) and thioalkyl substituted complexes **2f** and **2h** (entries 7 and 9) have yellowish green hue of emission. Complexes **2g** and **2n** (entries 8 and 15) are more red-shifted and yellow-green emissions can be observed. The complex **2m** (entry 14) emits true yellow. All the alkoxy substituted complexes **2a**–**e** (entries 2–6) have blue hues of emission. It is also interesting to note that the parent green emitter Alq_3 (entry 1) has a relatively low color purity of emission (circa 42%) while all new 4-substituted Alq_3 derivatives have improved color purities (54–90%).

2.7. Tris-(4-hydroxypyridinoanthrene)aluminum

Tris-(4-hydroxypyridinoanthrene)aluminum **2o** (Fig. 5) has absorption maximum at 469 nm (entry 16). The strong bathochromic effect and the intense absorption (ε=32,000) are both results of long conjugation in the tetracyclic system.[10] Emission is slightly red-shifted compared with the parent Alq_3. Small Stokes' shift refers to small difference between the equilibrium geometries of the ground and the excited states. The extremely rigid tetracyclic structure can also explain the observed relatively high relative quantum yield of **2o**.[10a] Especially interesting observation is that chromaticity coordinates of compound **2o** are located near the spectrum locus in the chromaticity diagram and therefore the color purity is exceptionally high (92%).

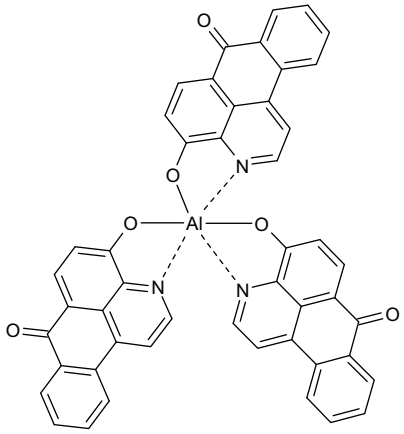

Figure 5. Tris-(4-Hydroxypyridinoanthrene)aluminum **2o**. The ligand has a rigid planar structure.

3. Conclusions

Alkoxy substituents at the 4-position of the 8-hydroxyquinoline ligand change notably the photophysical properties of the parent Alq_3. Both absorption and emission wavelengths are strongly blue-shifted and the optical band gap energy rises from 3.18 eV in the parent Alq_3 to about 3.4 eV in the alkoxy substituted Alq_3 derivatives. The maximum emission wavelength of the 4-substituted Alq_3 derivatives can be predicted from Hammett σ_p constants of the substituents. Substitution of the 4-position also improves the color purity of the emission and affects strongly the quantum yield. A linear correlation between Hammett σ_p constants of aryl and thioalkyl substituents and the PL quantum yields of Alq_3 derivatives has been observed. The combined relatively good quantum yield and high molar absorptivity together with a high emission color purity in a new kind of substituted Alq_3 derivative, tris-(4-hydroxypyridinoanthrene)aluminum, makes this compound interesting research target for further investigations.

4. Experimental section

4.1. General procedure for synthesis of aluminum complexes

Method A: ligand (3 equiv) and aluminum isopropoxide, $(C_3H_7O)_3Al$, (1 equiv) were mixed in methanol. The mixture was refluxed under nitrogen atmosphere for 21 h. The reaction mixture was cooled on ice bath and the precipitate was filtered. The solid product was washed with *n*-hexane (20 mL) and dried in a desiccator. Method B: ligand (3 equiv), anhydrous K_2CO_3 (3 equiv), and aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$, (1 equiv) were mixed in alcohol. The mixture was refluxed under nitrogen atmosphere. The work-up procedures are reported individually for each compound.

*4.1.1. Tris-(4-methoxy-8-hydroxyquinoline)aluminum (**2a**).* Compound **2a** was synthesized using method A. The specific amounts of chemicals used were: 4-methoxy-8-hydroxyquinoline **1a** (150 mg, 0.856 mmol), aluminum isopropoxide (59.3 mg, 0.290 mmol), and methanol (7 mL). The procedure afforded the title compound (106 mg, 68%) as a white powder. ^{1}H NMR (200 MHz, DMSO-d_6)

δ=4.01–4.05 (9H, m), 6.70 (1H, d, J=7.6 Hz), 6.81–6.99 (3H, m), 7.04 (1H, d, J=5.9 Hz), 7.13–7.26 (5H, m), 7.36–7.45 (3H, m), 8.44 (1H, d, J=5.8 Hz), 8.56 (1H, d, J=5.8 Hz). HRMS: calcd for $C_{30}H_{25}N_3O_6Al$ ($[M+H]^+$) 550.1559, found 550.1571.

*4.1.2. Tris-(4-butoxy-8-hydroxyquinoline)aluminum (**2b**).* Compound **2b** was synthesized using method A. The specific amounts of chemicals used were: 4-butoxy-8-hydroxyquinoline **1b** (150 mg, 0.690 mmol), aluminum isopropoxide (47.3 mg, 0.232 mmol), and methanol (7 mL). The procedure afforded the title compound (124 mg, 80%) as a white powder. ^{1}H NMR (200 MHz, DMSO-d_6) δ=0.90–0.98 (9H, m), 1.39–1.57 (6H, m), 1.77–1.84 (6H, m), 4.16–4.23 (6H, m), 6.69 (1H, d, J=7.2 Hz), 6.80–6.97 (3H, m), 7.01 (1H, d, J=5.9 Hz), 7.10–7.23 (5H, m), 7.34–7.44 (3H, m), 8.41 (1H, d, J=5.7 Hz), 8.52 (1H, d, J=5.7 Hz). HRMS: calcd for $C_{39}H_{43}N_3O_6Al$ ($[M+H]^+$) 676.2967, found 676.2961.

*4.1.3. Tris-(4-octyloxy-8-hydroxyquinoline)aluminum (**2c**).* Compound **2c** was synthesized using method A. The specific amounts of chemicals used were: 4-octyloxy-8-hydroxyquinoline **1c** (150 mg, 0.549 mmol), aluminum isopropoxide (37.0 mg, 0.181 mmol), and methanol (7 mL). The procedure afforded the title compound (120 mg, 79%) as a white powder. ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.84–0.89 (9H, m), 1.27–1.50 (30H, m), 1.79–1.96 (6H, m), 3.99–4.24 (6H, m), 6.42 (1H, d, J=5.8 Hz), 6.59 (1H, d, J=5.8 Hz), 6.64 (1H, d, J=5.8 Hz), 7.00–7.08 (3H, m), 7.17 (1H, d, J=5.7 Hz) 7.21–7.28 (3H, m), 7.34–7.43 (3H, m), 8.62–8.66 (2H, m). HRMS: calcd for $C_{51}H_{67}N_3O_6Al$ ($[M+H]^+$) 844.4845, found 844.4815.

*4.1.4. Tris-(4-iso-propyloxy-8-hydroxyquinoline)aluminum (**2d**).* Compound **2d** was synthesized using method A. The specific amounts of chemicals used were: 4-isopropyloxy-8-hydroxyquinoline **1d** (151 mg, 0.743 mmol), aluminum isopropoxide (50.3 mg, 0.246 mmol), and methanol (7 mL). The procedure afforded the title compound (76.4 mg, 49%) as a white powder. ^{1}H NMR (200 MHz, DMSO-d_6) δ=1.32–1.46 (18H, m), 4.81–5.00 (3H, m), 6.67 (1H, d, J=7.5 Hz), 6.81 (2H, d, J=7.5 Hz), 6.92 (1H, d, J=6.1 Hz), 7.06 (1H, d, J=6.1 Hz), 7.11–7.20 (5H, m), 7.33–7.41 (3H, m), 8.41 (1H, d, J=5.8 Hz), 8.52 (1H, d, J=5.8 Hz). HRMS: calcd for $C_{36}H_{37}N_3O_6Al$ ($[M+H]^+$) 634.2498, found 634.2491.

*4.1.5. Tris-(4-benzyloxy-8-hydroxyquinoline)aluminum (**2e**).* Compound **2e** was synthesized using method A. The specific amounts of chemicals used were: 4-benzyloxy-8-hydroxyquinoline **1e** (150 mg, 0.597 mmol), aluminum isopropoxide (40.4 mg, 0.198 mmol), and methanol (7 mL). The procedure afforded the title compound (107 mg, 69%) as a white powder. ^{1}H NMR (200 MHz, DMSO-d_6) δ=5.31–5.45 (6H, m), 6.72 (1H, d, J=6.9 Hz), 6.82–6.88 (2H, m), 6.99 (1H, d, J=5.9 Hz), 7.13–7.26 (6H, m), 7.35–7.55 (18H, m), 8.44 (1H, d, J=5.7 Hz), 8.56 (1H, d, J=5.7 Hz). HRMS: calcd for $C_{48}H_{36}N_3O_6NaAl$ ($[M+Na]^+$) 800.2317, found 800.2336.

*4.1.6. Tris-(4-n-propylthio-8-hydroxyquinoline)aluminum (**2f**).* Compound **2f** was synthesized using method B. The specific amounts of chemicals used were: 4-*n*-propylthio-8-hydroxyquinoline **1f** (102 mg, 0.465 mmol), K_2CO_3 (63.1 mg, 0.457 mmol), $Al(NO_3)_3\cdot 9H_2O$ (58.0 mg, 0.155 mmol), and ethanol (10 mL). The mixture was refluxed under nitrogen atmosphere for 21 h. The reaction mixture was cooled on ice bath. The resulting precipitate was filtered and washed sequentially with cold ethanol (5 mL), distilled water (5 mL), and cold ethanol (5 mL). The product was dried at 60 °C over night. The procedure afforded the title compound (91.4 mg, 87%) as a yellow powder. ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.01–1.13 (9H, m), 1.70–1.87 (6H, m), 2.91–3.06 (6H, m), 6.88 (1H, d, J=5.4 Hz), 7.01–7.20 (9H, m), 7.38–7.48 (3H, m), 8.54–8.60 (2H, m). HRMS: calcd for $C_{36}H_{36}N_3O_3NaAlS_3$ ($[M+Na]^+$) 704.1632, found 704.1653.

*4.1.7. Tris-(4-iso-propylthio-8-hydroxyquinoline)aluminum (**2g**).* Compound **2g** was synthesized using method B. The specific amounts of chemicals used were: 4-*iso*-propylthio-8-hydroxyquinoline **1g** (101 mg, 0.461 mmol), K_2CO_3 (63.5 mg, 0.459 mmol), $Al(NO_3)_3\cdot 9H_2O$ (57.2 mg, 0.152 mmol), and ethanol (10 mL). The mixture was refluxed under nitrogen atmosphere for 21 h. The work-up procedure was same as for **2f**. The procedure afforded the title compound (93.0 mg, 89%) as a light yellow powder. ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.38–1.52 (18H, m), 3.50–3.72 (3H, m), 6.92 (1H, d, J=5.4 Hz), 6.99–7.19 (9H, m), 7.38–7.48 (3H, m), 8.55–8.60 (2H, m). HRMS: calcd for $C_{36}H_{37}N_3O_3AlS_3$ ($[M+H]^+$) 682.1812, found 682.1824.

*4.1.8. Tris-(4-n-butylthio-8-hydroxyquinoline)aluminum (**2h**).* Compound **2h** was synthesized using method B. The specific amounts of chemicals used were: 4-*n*-butylthio-8-hydroxyquinoline **1h** (100 mg, 0.429 mmol), K_2CO_3 (59.7 mg, 0.432 mmol), $Al(NO_3)_3\cdot 9H_2O$ (54.3 mg, 0.145 mmol), and ethanol (10 mL). The mixture was refluxed under nitrogen atmosphere for 21 h. The work-up procedure was same as for **2f**. The procedure afforded the title compound (84.8 mg, 82%) as a yellow powder. ^{1}H NMR (200 MHz, DMSO-d_6) δ=0.85–0.94 (9H, m), 1.37–1.50 (6H, m), 1.59–1.77 (6H, m), 3.09–3.20 (6H, m), 6.73 (1H, d, J=7.5 Hz), 6.87 (2H, d, J=7.8), 7.07–7.15 (3H, m), 7.18 (1H, d, J=5.4 Hz), 7.31 (1H, d, J=5.6 Hz), 7.37–7.53 (5H, m), 8.37 (1H, d, J=5.4 Hz), 8.48 (1H, d, J=5.4 Hz). HRMS: calcd for $C_{39}H_{42}N_3O_3NaAlS_3$ ($[M+Na]^+$) 746.2101, found 746.2067.

*4.1.9. Tris-(4-phenyl-8-hydroxyquinoline)aluminum (**2i**).* Compound **2i** was synthesized using method B. The specific amounts of chemicals used were: 4-phenyl-8-hydroxyquinoline **1i** (49.8 mg, 0.225 mmol), K_2CO_3 (31.0 mg, 0.224 mmol), $Al(NO_3)_3\cdot 9H_2O$ (29.0 mg, 0.077 mmol), and methanol (10 mL). The mixture was refluxed under nitrogen atmosphere for 23 h. The reaction mixture was cooled on ice bath. The resulting precipitate was filtered and washed sequentially with cold methanol (5 mL) and distilled water (2.5 mL). The product was dried at 60 °C over night. The procedure afforded the title compound (33.1 mg, 64%) as a yellow powder. ^{1}H NMR (200 MHz, DMSO-d_6) δ=6.83 (1H, d, J=6.83 Hz), 6.97–7.13 (5H, m), 7.43–7.71 (22H, m), 8.72 (1H, d, J=5.2 Hz), 8.88 (1H, d, J=4.7 Hz). HRMS: calcd for $C_{45}H_{30}N_3O_3NaAl$ ($[M+Na]^+$) 710.2000, found 710.1983.

*4.1.10. Tris-(4-p-methylphenyl-8-hydroxyquinoline)aluminum (**2j**).* Compound **2j** was synthesized using method B. The specific amounts of chemicals used were: 4-*p*-methylphenyl-8-hydroxyquinoline **1j** (100 mg, 0.425 mmol), K_2CO_3 (59.3 mg, 0.429 mmol), $Al(NO_3)_3\cdot 9H_2O$ (53.2 mg, 0.142 mmol), and ethanol (10 mL). The mixture was refluxed under nitrogen atmosphere for 21 h. The reaction mixture was cooled on ice bath and distilled water (5 mL) was added. The resulting precipitate was filtered and washed with cold ethanol (10 mL). The product was dried at 60 °C over night. The procedure afforded the title compound (50.1 mg, 48%) as a yellow powder. ^{1}H NMR (200 MHz, DMSO-d_6) δ=2.41 (9H, s), 6.81 (1H, d, J=7.5 Hz), 6.97 (2H, d, J=7.5 Hz), 7.04–7.14 (3H, m), 7.32–7.55 (18H, m), 7.65 (1H, d, J=5.0 Hz), 8.69 (1H, d, J=5.0 Hz), 8.84 (1H, d, J=4.9 Hz). HRMS: calcd for $C_{48}H_{37}N_3O_3Al$ ($[M+H]^+$) 730.2650, found 730.2636.

*4.1.11. Tris-(4-o-methylphenyl-8-hydroxyquinoline)aluminum (**2k**).* Compound **2k** was synthesized using method B. The specific amounts of chemicals used were: 4-*o*-methylphenyl-8-hydroxyquinoline **1k** (101 mg, 0.429 mmol), K_2CO_3 (58.9 mg, 0.426 mmol), $Al(NO_3)_3\cdot 9H_2O$ (54.1 mg, 0.144 mmol), and ethanol (10 mL). The mixture was refluxed under nitrogen atmosphere for 21 h. The reaction mixture was cooled on ice bath. The resulting precipitate

was filtered and washed sequentially with cold ethanol (5 mL), distilled water (2.5 mL), and cold ethanol (5 mL). The product was dried at 60 °C over night. The procedure afforded the title compound (48.5 mg, 46%) as a yellow powder. HRMS: calcd for $C_{48}H_{37}N_3O_3Al$ ($[M+H]^+$) 730.2650, found 730.2667.[18]

*4.1.12. Tris-(4-p-methoxyphenyl-8-hydroxyquinoline)aluminum (**2l**).* Compound **2l** was synthesized using method B. The specific amounts of chemicals used were: 4-*p*-methoxyphenyl-8-hydroxyquinoline **1l** (100 mg, 0.398 mmol), K_2CO_3 (58.9 mg, 0.426 mmol), $Al(NO_3)_3 \cdot 9H_2O$ (53.2 mg, 0.142 mmol), and ethanol (10 mL). The mixture was refluxed under nitrogen atmosphere for 21 h. The reaction mixture was cooled on ice bath and distilled water (5 mL) was added. The resulting precipitate was filtered and washed with cold ethanol (10 mL). The product was dried at 60 °C over night. The procedure afforded the title compound (84.9 mg, 82%) as a yellow powder. ^{1}H NMR (200 MHz, DMSO-d_6) δ=3.84 (9H, s), 6.80 (1H, d, J=7.4 Hz), 6.96 (2H, d, J=7.7 Hz), 7.09–7.17 (9H, m), 7.38 (1H, d, J=5.1 Hz), 7.47–7.64 (12H, m), 8.67 (1H, d, J=5.0 Hz), 8.82 (1H, d, J=5.0 Hz). HRMS: calcd for $C_{48}H_{36}N_3O_6NaAl$ ($[M+Na]^+$) 800.2317, found 800.2292.

*4.1.13. Tris-(4-p-cyanophenyl-8-hydroxyquinoline)aluminum (**2m**).* Compound **2m** was synthesized using method B. The specific amounts of chemicals used were: 4-*p*-cyanophenyl-8-hydroxyquinoline **1m** (100 mg, 0.406 mmol), K_2CO_3 (56.2 mg, 0.407 mmol), $Al(NO_3)_3 \cdot 9H_2O$ (51.5 mg, 0.137 mmol), and 2-mehyl-2-butanol (10 mL). The mixture was refluxed under nitrogen atmosphere for 21 h. The reaction mixture was cooled on ice bath. The resulting precipitate was filtered and washed sequentially with cold ethanol (5 mL), distilled water (5 mL), cold ethanol (5 mL), and petrol (20 mL). The product was dried at 60 °C over night. The procedure afforded the title compound (77.5 mg, 75%) as a dark yellow powder. ^{1}H NMR (200 MHz, DMSO-d_6) δ=6.82–7.02 (6H, m), 7.45–7.63 (6H, m), 7.72–7.85 (7H, m), 8.05 (6H, d, J=7.5 Hz), 8.74 (1H, d, J=4.6 Hz), 8.89 (1H, d, J=4.5 Hz). HRMS: calcd for $C_{48}H_{28}N_6O_3Al$ ($[M+H]^+$) 763.2038, found 763.2025.

*4.1.14. Tris-(4-o-ethoxycarbonylphenyl-8-hydroxyquinoline)aluminum (**2n**).* Compound **2n** was synthesized using method B. The specific amounts of chemicals used were: 4-*o*-ethoxycarbonylphenyl-8-hydroxyquinoline **1n** (100 mg, 0.341 mmol), K_2CO_3 (47.1 mg, 0.341 mmol), $Al(NO_3)_3 \cdot 9H_2O$ (42.8 mg, 0.114 mmol), and ethanol (10 mL). The mixture was refluxed under nitrogen atmosphere for 24 h. The reaction mixture was concentrated by evaporator. The concentrate was slowly added to petrol (15 mL) and the mixture was cooled on ice bath. The resulting precipitate was filtered and washed sequentially with the mixture of petrol and ethanol (20:1, 5 mL), distilled water (5 mL) and again with petrol/ethanol solution (5 mL). The product was dried at 60 °C over night. The procedure afforded the title compound (76.8 mg, 75%) as a dark yellow powder. ^{1}H NMR (200 MHz, DMSO-d_6) δ=−0.31 to 1.08 (9H, m), 3.46–3.98 (6H, m), 6.42–6.95 (6H, m), 7.33–8.04 (19H, m), 8.70–8.90 (2H, m). HRMS: calcd for $C_{54}H_{43}N_3O_9Al$ ($[M+H]^+$) 904.2815, found 904.2792.

*4.1.15. Tris-(4-hydroxypyridinoanthrene)aluminum (**2o**).* Compound **2o** was synthesized using method B. The specific amounts of chemicals used were: 4-hydroxypyridinoanthrene **1o** (97.6 mg, 0.395 mmol), K_2CO_3 (56.1 mg, 0.406 mmol), $Al(NO_3)_3 \cdot 9H_2O$ (51.2 mg, 0.136 mmol), and ethanol (10 mL). The mixture was refluxed under nitrogen atmosphere for 21 h. The hot reaction mixture was filtered and the precipitate was washed sequentially with cold ethanol (5 mL), distilled water (5 mL), and cold ethanol (5 mL). The precipitate was dried at 60 °C over night. The procedure afforded the title compound (78.3 mg, 78%) as an orange powder. ^{1}H NMR (200 MHz, DMSO-d_6) δ=6.95–7.28 (3H, m), 7.71–7.85 (7H, m), 8.25–8.56 (11H, m), 8.81 (2H, d, J=4.4 Hz), 8.98 (1H, d, J=4.6 Hz). HRMS: calcd for $C_{48}H_{24}N_3O_6NaAl$ ([M+Na]) 788.1378, found 788.1392.

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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.2009.07.057.

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