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PAPER

Fused Alq_3 derivatives: syntheses and photophysical characteristics†

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Three new tetracyclic 8-hydroxyquinoline derivatives were synthesized by using a Pd catalyzed intramolecular direct arylation reaction in a key step. Furthermore, the new compounds were used as ligands in aluminium complexes and their photophysical properties were studied in detail both in solution and solid state by using absorption, steady-state, and time resolved fluorescence spectroscopies. Results show especially that the aluminium complex of 11*H*-indolo[3,2-*c*]quinolin-4-ol has the most blue-shifted emission maximum among the Alq_3 derivatives to date and CIE chromaticity coordinates locate on the deep blue area (0.16, 0.12). Moreover, the fluorescence quantum yield of this compound is 3.1–3.5 times higher compared with the parent Alq_3. Photophysical properties of the complex did not show major differences between the solution and the solid states. The lack of melting endotherm in DSC analysis indicates that the compound is amorphous. Based on the results, 11*H*-indolo[3,2-*c*]quinolin-4-ol has promising features to be applied as a ligand for aluminium or other metal ions in different applications.

1. Introduction

8-Hydroxyquinoline is a bidentate ligand, which forms complexes effectively with various metal ions. Tris-(8-hydroxyquinoline) aluminium (Alq_3) (Fig. 1) is a fluorescent octahedral complex compound, which was used as a combined electron transport and emitter layer in organic light emitting diode (OLED) devices for the first time by Tang and VanSlyke in 1987.[1] Since that, the parent Alq_3 has become a standard material in OLED devices. The parent Alq_3 has also found an important role in the device architectures of organic solar cells. It has been used as an effective buffer layer to prohibit undesired cathode diffusion from a metal cathode to an organic layer and to increase the lifetime of devices by preventing penetration of oxygen and moisture.[2] Moreover, doping of Alq_3 in either the donor or acceptor layer has been observed to improve organic photovoltaic (OPV) cell performance by increasing *e.g.* the power conversion efficiency.[3] The parent Alq_3 has also been shown to work as a host material in an organic solar concentrator in which Alq_3 provides a polar environment for a highly polar excited state of the dye molecule thus reducing concentration quenching.[4]

Theoretical studies have shown that the lowest unoccupied molecular orbital (LUMO) of the parent Alq_3 is located mainly on the pyridyl side of the organic ligand and the highest occupied molecular orbital (HOMO) on the phenoxide side.[5] This observation has been a key in the development of new derivatives with tailored photophysical properties. It has been experimentally shown that emission properties can be effectively and systematically tuned by substituting either the 4-position or the 5-position of the quinoline ring.[6] In very recent studies, it has been shown that an amorphous tris-(4-piperidinyl-8-hydroxyquinoline) aluminium (Fig. 1) works as a superior emitting material in OLED devices and tris-(5-fluoro-8-hydroxyquinoline)aluminium can increase device efficiency considerably when it is used as an electron transport material in the Si-anode based OLED.[7]

Substituting a polymerizable unit to 8-hydroxyquinoline allows the incorporation of a Alq_3 derivative into the polymer

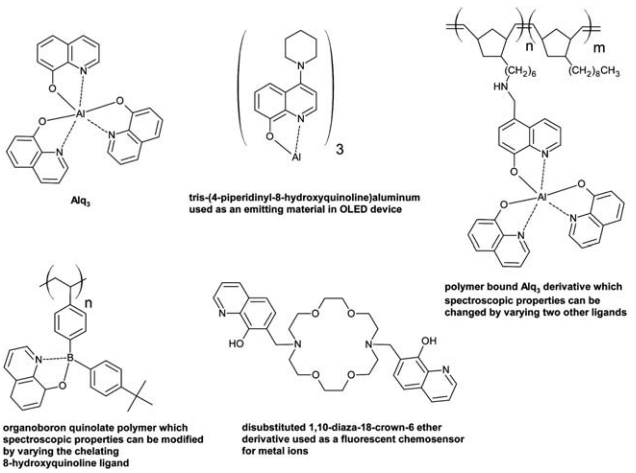

Fig. 1 8-Hydroxyquinoline and its derivatives as chelating ligands.

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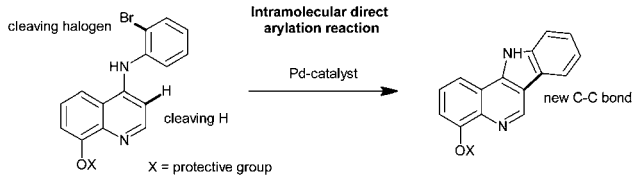


Scheme 1 Intramolecular Pd-catalyzed C-C bond formation

backbone and emission properties of that Alq_3-functionalized polymer can be tuned by alternating the substituents in the 8-hydroxyquinoline ligand (Fig. 1).[8] Polymers with 8-hydroxyquinoline side chains can also complex boron in addition to aluminium.[9] Such boron quinolate-functionalized copolymers have shown excellent emission properties and high electron mobilities.[9b] A slightly different approach utilizes poly(bromo-*p*-*tert*-butylphenylborylstyrene) to complex 8-hydroxyquinoline (Fig. 1) and its derivatives.[10] This methodology allows tuning the chemical, physical, and photophysical properties simply by varying the chelating 8-hydroxyquinoline ligand.

Also other highly versatile application possibilities have increased researchers' interest to apply 8-hydroxyquinoline and develop synthetic methods to produce its new derivatives. Those applications cover for example near-infrared emitting tris-(8-hydroxyquinoline)lanthanide-functionalized mesoporous silica materials as well as *N*,*N*′-bis((8-hydroxy-7-quinolinyl)methyl)-1,10-diaza-18-crown-6 ether (Fig. 1) and its substituted derivatives, which can be used as fluorescent chemosensors for different divalent metal ions such as magnesium.[11] Experimental research including design and synthesis of new compounds is essential in order to obtain exact knowledge about luminescence and other photophysical properties of the compounds, because theoretical methods often give just rough estimations or trends.[12]

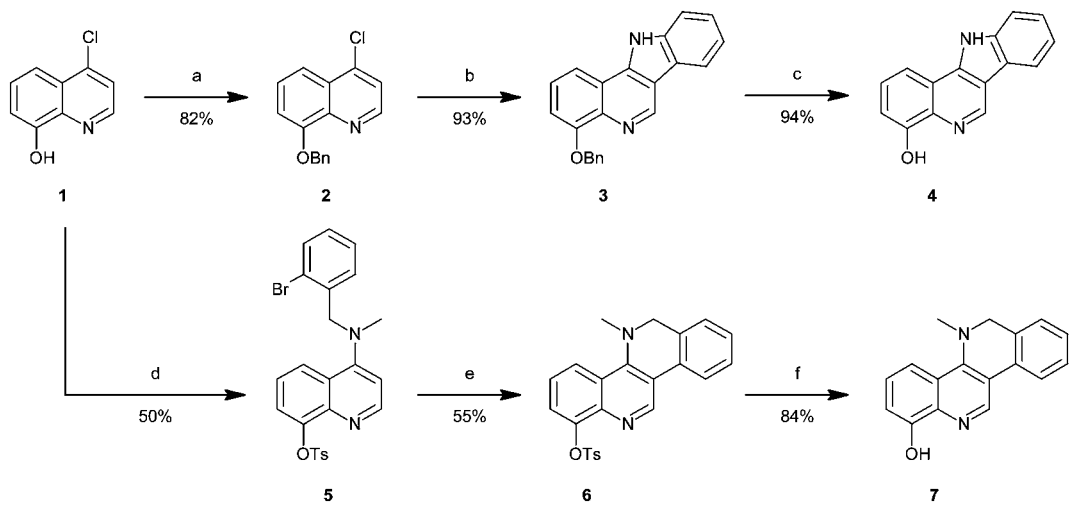
In this paper, we present a novel strategy to synthesize new tetracyclic 8-hydroxyquinoline derivatives by using a Pd-catalyzed direct arylation in a key reaction step (Scheme 1). These new 8-hydroxyquinoline derivatives were applied as ligands for aluminium and spectroscopic properties of the resulting Alq_3 derivatives were studied in detail both in solution and solid state by using absorption, steady-state, and time resolved fluorescence spectroscopy. Especially, tris-(11*H*-indolo[3,2-*c*]quinolin-4-ol) aluminium showed interesting properties compared with the parent Alq_3: three times higher photoluminescence quantum yield and deep blue emission with CIE (Commission internationale de l'éclairage) coordinates (0.16, 0.12). This is the most blue-shifted emission among the Alq_3 derivatives so far and the differential scanning calorimetry (DSC) data indicate that the complex is amorphous. These properties make the Alq_3 derivative and the synthesized ligand itself especially interesting for different applications *e.g.* blue emission utilizing full-color display and lighting applications.

2. Results and discussion

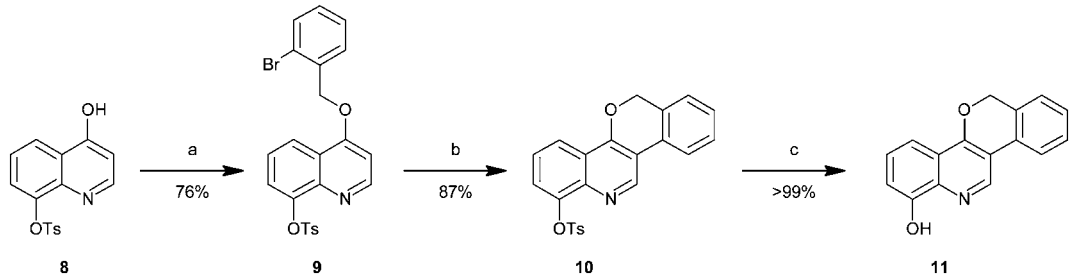
2.1 Syntheses

4-Chloro-8-hydroxyquinoline **1** (Scheme 2) was synthesized by using a previously reported method.[13] On the first reaction step, the hydroxyl group was protected with the benzyl group by reacting compound **1** with benzyl bromide. 8-(Benzyloxy)-4-chloroquinoline **2** was collected in good yield (82%) after flash chromatography.

In the literature, Fisher indole synthesis and ligand free Pd-catalyzed arylation have been used to construct the 11*H*-indol [3,2-*c*]quinoline skeleton.[14] Both methods gave the desired products in relatively low yields. Far more efficient method has been presented lately by Maes *et al.*[15] In their method, intermolecular amination and intramolecular arylation are carried out by using auto-tandem catalysis and product yields varying from moderate to high (52–82%). Our synthetic protocol applies the solvent free amination reaction and Pd-catalyzed direct arylation method. Amination was performed by heating compound **2** in 2-bromoaniline for 17 h. Pd-catalyzed intramolecular direct arylation was done by using $Pd(OAc)_2$ as a palladium source for the



Scheme 2 *Reagents and conditions*: (a) (i) K_2CO_3 (2 equiv), DMF rt, 10 min; (ii) BnBr (1.1 equiv), rt, 18 h; (b) (i) 2-bromoaniline (10 equiv) 135 °C, 17 h; (ii) NaOH (aq) (3 equiv), acetone, reflux, 10 min; (iii) Pd(OAc) (5 mol%), PCy_3-HBF_4 (10 mol%), anhydrous K_2CO_3 (2.5 equiv), DMA 160 °C, 3 h; (c) Pd–C (10 wt%), H_2, ethanol, reflux, 5 h; (d) (i) 2-bromo-*N*-methylbenzylamine (6.25 equiv) 135 °C, 17 h; (ii) HCl (aq); (iii) NaOH (aq) (2 equiv), reflux, 15 min; (iv) TsCl (1 equiv), acetone rt, 1 h; (e) Pd(OAc) (10 mol%), PCy_3-HBF_4 (20 mol%), anhydrous K_2CO_3 (2.5 equiv), DMA 160 °C, 4 h; (f) (i) NaOH (aq) (5 equiv), ethanol, reflux, $2^1/_2$ h; (ii) HCl (aq).



Scheme 3 *Reagents and conditions*: (a) (i) NaH (1.7 equiv), DMF rt, 5 min; (ii) 2-bromobenzyl bromide (1.5 equiv), rt, 24 h; (b) Pd(OAc) (5 mol%), PCy_3-HBF_4 (10 mol%), anhydrous K_2CO_3 (2.5 equiv), DMA 160 °C, 3 h; (c) (i) NaOH (aq) (3 equiv), ethanol/acetone, reflux, $2^1/_2$ h; (ii) HCl (aq).

catalysis. Air stable tricyclohexylphosphine tetrafluoroborate (PCy_3-HBF_4) was used as a ligand and anhydrous K_2CO_3 as a base. The same catalyst system has successfully been used in various direct arylation reactions earlier by Fagnou *et al.*[16] Reaction was monitored by thin layer chromatography (TLC) analysis and it was observed that the use of 5 mol% catalyst loading of $Pd(OAc)_2$ gave total conversion of the starting material within three hours.[17] As a noteworthy observation, it must be mentioned that it was necessary to protect the 8-hydroxyl group before direct arylation reaction. Product formation could not be observed when direct arylation was tried right away after amination of compound **1**. The tetracyclic quinoline derivative 4-benzyloxy-11*H*-indol[3,2-*c*]quinoline **3** was collected in high yield (93%). Pd catalyzed hydrogenolysis of compound **3** was carried out by using standard Pd–C (10 wt%) in ethanol under H_2 atmosphere. The procedure gave the final ligand **4** in excellent yield (94%).

Compound **5** (Scheme 2) was prepared from compound **1** by performing solvent free amination and tosylation reactions consecutively. Compound **5** was collected as a pure product in moderate yield (50%). Direct arylation of compound **5** was accomplished by using 10 mol% of Pd catalyst and compound **6** was collected in 55% yield. Finally, detosylation of compound **6** gave the desired ligand **7** in high yield (84%) by using NaOH as a deprotection agent.

4-Hydroxy-8-tosyloxyquinoline[18,19] **8** (Scheme 3) is readily available and can be used as a starting material in the synthesis of ligand **11**. Alkylation of compound **8** in the presence of NaH and 2-bromobenzyl bromide gave product **9** in good yield (76%). Direct arylation of compound **9** was performed by using the same method as for compound **2**. Tetracyclic quinoline derivative **10** was collected in good yield (87%). Deprotection of compound **10** with NaOH gave ligand **11** in quantitative yield (>99%).

Complexes **12–14** (Fig. 2) were synthesized by using a previously reported method.[6a] New Alq_3 derivatives were isolated in good to high yields (72–92%). ^{1}H NMR spectra show that also the new derivatives exist as their meridional isomers similarly as the parent Alq_3 in solution at room temperature.[20]

2.2 Photophysical properties in solution

Absorption and emission (photoluminescence) spectra in the steady state for the parent Alq_3 and its derivatives (**12–14**) in solution are shown in Fig. 3. Because of different solubility properties between the prepared complexes, compound **12** was measured in ethanol and compounds **13** and **14** in chloroform. Reference solutions of the parent Alq_3 were prepared in both solvents. Fluorescence lifetimes (τ) and corresponding amplitudes (A) were obtained by using the time correlated single photon counting (TCSPC) method. Measuring the decay curves at a wide range of wavelengths provides an alternative way to determine the ratio of emitted and absorbed photons (*i.e.* quantum yield) for each compound. τ was assumed to be constant at each monitoring wavelength and the amplitudes were obtained from the fittings of the decay curves at each wavelength

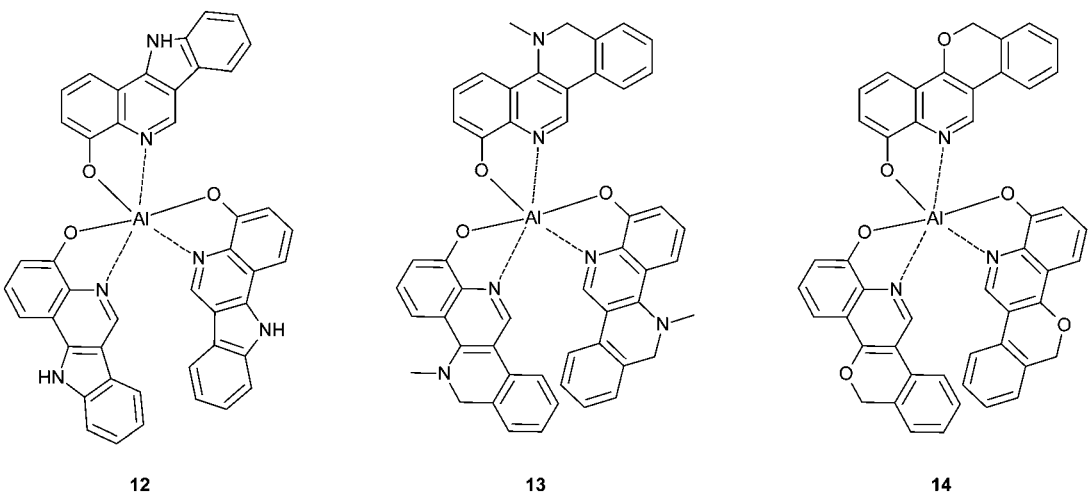


Fig. 2 The chemical structures of the fused Alq_3 derivatives **12–14**.

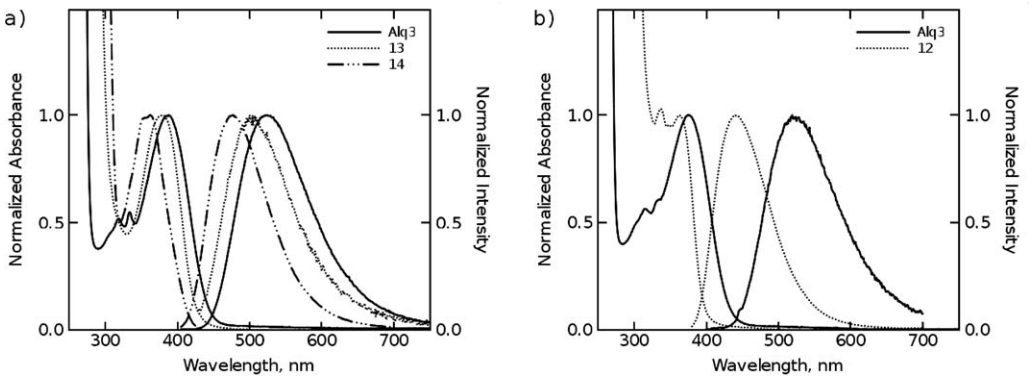


Fig. 3 Normalized steady state spectra in diluted solutions: absorption and emission of the parent Alq_3 and fused derivatives **13** and **14** in $CHCl_3$ (a), and the parent Alq_3 and **12** in EtOH (b). Emission band features were independent of the excitation wavelength.

and corrected according to the detectors wavelength sensitivity. The product of τ and the corresponding amplitude was summed throughout the measured range ($\Sigma A\tau$), which gives the quantum yields referred to the parent Alq_3. In the time resolved experiment, transmittance ($T = 1 - 10^{-Abs.}$) was not equal for all the samples at the excitation wavelength of 340 nm. Thus, this was taken into account in calculations. Measured lifetimes (Table 1) for the parent Alq_3 in $CHCl_3$ and in ethanol are comparable with the values reported in the literature.[21] Absolute data, which were used in the determination of relative quantum yields, are shown in the ESI† together with the decay curves, decay associated spectra and calculation procedures.

Generally, increased degree of conjugation causes the bathochromic effect.[22] However, compounds **12–14** have blue-shifted absorption maxima (*i.e.* hypsochromic effect) and increased molar extinction coefficients (*i.e.* hyperchromic effect) compared with those of Alq_3. The strong electron donating group (EDG) at the 4-position of the quinoline ring seems to have a major contribution to the absorption profile instead of the extended conjugation sphere caused by the attached phenyl ring at the 3-position.

Tris-(11*H*-indolo[3,2-*c*]quinolin-4-ol)aluminium **12** has in ethanol 3.1–3.5 times higher fluorescence quantum yield (Φ) than the parent Alq_3. Fluorescence lifetime (τ) is somewhat shorter compared to that with Alq_3. By using the relative fluorescence quantum yields and measured fluorescence lifetimes in Table 1, one can calculate that the radiative rate constant for **12** is 3.5 times higher than that for Alq_3. In addition, taking into account the absolute fluorescence quantum yield of Alq_3 in ethanol (0.116[21]) the absolute fluorescence quantum yield for **12** is 0.35 and the radiative fluorescence rate constants are $1.3 \times 10^7\ s^{-1}$ and $4.6 \times 10^7\ s^{-1}$ for Alq_3 and **12**, respectively. Simultaneously with the increased radiative fluorescence rate the non-radiative rate constant of **12** ($8.3 \times 10^7\ s^{-1}$) decreased compared with Alq_3 ($9.8 \times 10^7\ s^{-1}$).

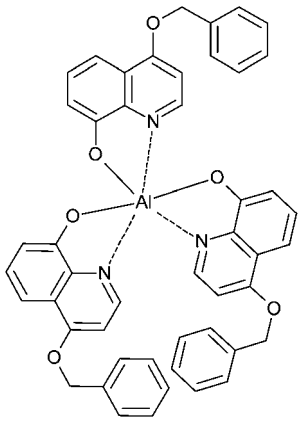
In terms of CIE chromaticity coordinates (0.16, 0.12), compound **12** shows deep blue emission. To the best of our knowledge, the observed 77 nm blue-shift is the largest among the Alq_3 derivatives so far.[23] Previously, it has been theoretically predicted that attachment of EDG on the 4-position of the quinoline ring causes rise of LUMO level leading to a wider energy gap, and thus causing the blue-shifted emission.[5] LUMO also has a notable coefficient at the 3-position.[24] This can be the reason for the exceptionally high blue-shift of compound **12**, in which a strong electron donating nitrogen part at the 4-position is also fully conjugated to the 3-position. On the other hand, electron donating nitrogen and oxygen parts at the 4-position in compounds **13** and **14** are isolated from the phenyl part attached on the 3-position, which can be considered as an electron neutral substituent in terms of Hammett substituent constants.[25] Thus the phenyl part at the 3-position is likely to increase the conjugation of the quinoline ring, but does not shift electron density from the electron donating part at the 4-position in compounds **13** and **14**.

For compound **13** in chloroform, the relative fluorescence quantum yields obtained both in the steady state and by the time-resolved method are much lower than the quantum yield of the parent Alq_3. Fluorescence maximum was only slightly blue-shifted and fluorescence decay was two exponential with

Table 1 Photophysical parameters of the parent Alq_3 and fused derivatives in solution

Compound	λ_{abs}[a]/nm	ε[b]	λ_{PL}[c]/nm	FWHM/nm	Φ[d]	Stokes' shift/cm^{-1}	τ[e]/ns	$\Sigma A\tau/(1-T)$[f]	CIE/(x, y)[g]
Alq_3[h]	378	7.6×10^3	519	117	1	7190	8.99	1	(0.32, 0.51)
Alq_3[i]	385	5.9×10^3	522	116	1	6820	16.63	1	(0.33, 0.52)
12[h]	362	1.5×10^4	442	81	3.06	5000	7.76	3.47	(0.16, 0.12)
13[i]	379	2.9×10^4	499	106	0.14	6350	9.73 (15%) 1.81 (85%)	0.34	(0.25, 0.41)
14[i]	362	1.9×10^4	478	92	1.45	6700	11.76	2.14	(0.18, 0.28)

[a] Absorption maximum. [b] Molar extinction coefficient. [c] Photoluminescence maximum. [d] Relative fluorescence quantum yield. (The absolute fluorescence quantum yields for Alq_3 in ethanol and chloroform are 0.116 and 0.223 respectively.[21]) [e] Fluorescence lifetime. [f] Relative fluorescence quantum yield by the TCSPC experiment (A = amplitude, T = transmittance). [g] CIE chromaticity coordinates. [h] In EtOH. [i] In $CHCl_3$.



λ_{PL} = 465 nm (in $CHCl_3$)
Φ = 0.66 (relative to Alq_3)

Fig. 4 The chemical structure of 4-alkoxy substituted Alq_3 derivative, tris-(4-benzyloxy-8-hydroxyquinoline)aluminium.[6a]

relative amplitudes of 0.15 and 0.85, and corresponding lifetimes of 9.7 ns and 1.8 ns, respectively. Obviously, a concomitant twisted intramolecular charge transfer (TICT) occurs which would explain the observed second decay component.[22] As was calculated for compound **12**, the absolute fluorescence quantum yields and radiative fluorescence rate constants can be determined for **13**. In chloroform, the absolute fluorescence quantum yield for **13** is 0.03 (0.223[21] for the parent Alq_3 in chloroform) and the radiative fluorescence rate constants are 1.3×10^7 s^{-1} and 1.0×10^7 s^{-1} for Alq_3 and **13**, respectively. The non-radiative fluorescence rate constant of **13** (3.2×10^8 s^{-1}) increased notably compared with Alq_3 (4.7×10^7 s^{-1}).

Relative to the parent Alq_3, emission maximum was blue-shifted 23 nm, but CIE coordinates (0.25, 0.41) are located still on the green area. Likely, the extended conjugation due to the phenyl ring is a reason for the observed blue-shift of compound **13** which is smaller than that of piperidinyl and 4-methyl piperazinyl substituted Alq_3 derivatives.[7a] In the case of compound **14**, emission maximum was blue-shifted 44 nm compared with the parent Alq_3. The observed blue-shift is the same order of magnitude than those of tris-(4-alkoxy-8-hydroxyquinoline) aluminium complexes (Fig. 4) reported earlier.[6a]

The relative fluorescence quantum yield for **14** is considerably higher compared with the parent Alq_3 and its unfused analogue, tris-(4-benzyloxy-8-hydroxyquinoline)aluminium[6a] (Fig. 4). The absolute fluorescence quantum yield in chloroform for **14** is 0.32 and the radiative and non-radiative fluorescence rate constants are 2.8×10^7 s^{-1} and 5.8×10^7 s^{-1}, respectively. Increased fluorescence quantum yield can be related to the fused tetracyclic structure of new derivatives. The C–C bond between the aryl group and the quinoline ring increases the rigidity of molecular structures, which explains the increased Φ of compounds **12** and **14**. Decreased Stokes' shifts of the fused derivatives can also be related to rigid molecular structures.[26]

2.3 Solid state properties

Solution processing is a highly desired method because it allows low-cost manufacturing techniques for organic electronic devices in the industrial scale. It has also become the current trend in organic light emitting diode and solar cell research.[27] Thus, we demonstrated deposition of the thin films of Alq_3 derivatives on the quartz substrate by using the spin coating technique. The first set of films was spin coated from a diluted solution (0.1 mM) and produced very weak absorption (Fig. 5a). Therefore, concentration was increased to 1 mM and another set of films was prepared. Reference film (9.5 nm) was made from the parent Alq_3 by evaporating in high vacuum, because a spin coated film of the parent Alq_3 showed neither detectable absorption nor emission. The results are shown in Fig. 5 and Table 2.

For an unknown reason, the thin film of compound **12** had very weak absorption (Fig. 5a and c). However, emission measurements yielded clear signals (Fig. 5b and d) corresponding to the ones observed in solutions (Fig. 3b). Compound **13** in thin film was invisible in all fluorescence measurements, despite relatively high absorbance of the layer (Fig. 5c). Fluorescence lifetimes in the solid state, when excited at 340 nm, were resolved only for the parent Alq_3 and compound **12**. Decays were fitted with the two-exponential model. The appearance of the fast component can be attributed to solid state interaction between the molecules, which is not taking place in dilute solutions. The two components have very similar lifetimes than what has been reported in the literature for 3 μm thick crystalline film, although the pre-exponential amplitudes were different.[21]

In terms of CIE coordinates, it is interesting to note that emission of the parent Alq_3 was shifted to the yellowish-green area while the solid state emission of compound **12** remained on the deep blue area. For compound **12**, the peak width (FWHM) values of the thin films (Table 2) are close to the one obtained in solution (Table 1) whereas FWHM values of the parent Alq_3 showed major difference between the two states. For compound **14**, the solid state emission spectrum was clearly broadened compared with the solution state spectrum, which indicates increased interaction between the molecules.[21]

DSC analyses indicate that the synthesized Alq_3 derivatives **12** and **13** are amorphous. The parent Alq_3 showed a sharp melting endotherm at 417 °C, which is consistent with earlier studies,[28] whereas a melting endotherm could not be detected for compounds **12** and **13** (Fig. 6). The parent Alq_3 showed a glass transition temperature (T_g) at 162 °C, which is lower compared with earlier reported values. Compounds **12** and **14** showed slightly lower T_g values of 142 and 153 °C, respectively, relative to Alq_3. Compound **14** showed also a sharp melting endotherm at 194 °C. Compound **13** can be considered thermally more stable than the parent Alq_3, because of the lack of a melting endotherm and a higher T_g of 173 °C. Generally, amorphous materials have advantage over crystalline materials in various organic electronic applications because of their good processability, homogeneity, higher quantum efficiency in the solid state and capability to form uniform films.[29]

In general, spin coating is not a well-suited processing technique for the studied solutions, because the thickness and uniformity of the resulting films could not be accurately controlled by using this method. However, results show the potential of new derivatives to form thin films and if suitable a deposition procedure is selected from the other available solution-processing methods such as spray-on deposition, ink-jet or roll-to-roll printing, the quality of films may be controlled

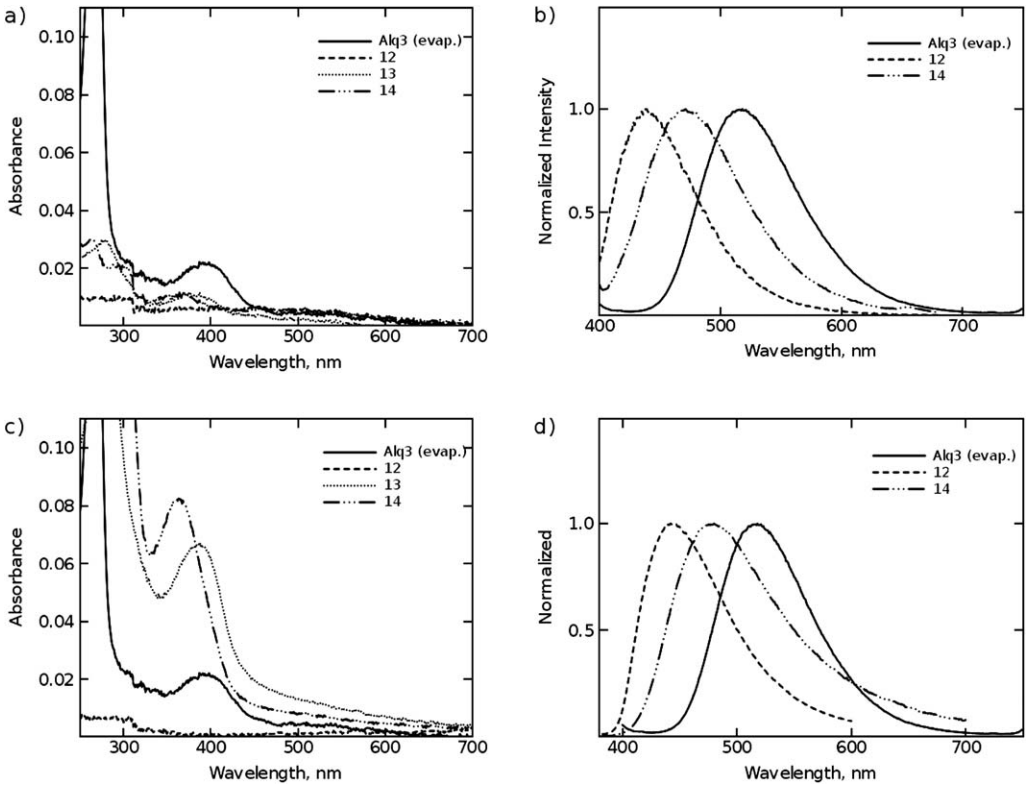


Fig. 5 Spectral characteristics of the parent Alq_3 and its fused derivatives **12–14** in thin films. Absorption (a and c) and emission (b and d) spectra of the parent Alq_3 (evaporated film, 9.5 nm), derivative **12** (spin coated from ethanol) and derivatives **13** and **14** (spin coated from chloroform) spinned from diluted solutions (0.1 mM, a and b) and concentrated solutions (1 mM, c and d) on quartz substrates. Emission band features were independent of the excitation wavelength.

Table 2 Photophysical parameters of the parent Alq_3 and fused derivatives in the solid state

Compound	λ_{abs}[a]/nm	λ_{PL}[b]/nm	FWHM/nm	τ_1[c]/ns	τ_2[d]/ns	τ_{avg}[e]/ns	CIE/(x, y)[f]
Alq_3[g]	387	518	93	27.00	6.76	10.77	(0.28, 0.53)
12	—	442	78,[h] 87[j]	3.81[j]	0.55[j]	0.77	(0.18, 0.16)
13	388	—	—	—	—	—	
14	363	480	95,[i] 112[k]	—	—	—	(0.23, 0.32)

[a] Absorption maximum. [b] Photoluminescence maximum. [c] Fluorescence lifetime, long-living component. [d] Fluorescence lifetime, short-living component. [e] Average fluorescence lifetime, $\tau_{avg} = (a_1\tau_1 + a_2\tau_2)/(a_1 + a_2)$. [f] CIE chromaticity coordinates. [g] Evaporated (9.5 nm). [h] Spin coated (0.1 mM in EtOH). [i] Spin coated (0.1 mM in $CHCl_3$). [j] Spin coated (1 mM in EtOH). [k] Spin coated (1 mM in $CHCl_3$).

more precisely. Especially, due to the observed deep blue emission of compound **12**, as well as the increased fluorescence quantum yield, one of the most likely application possibilities for that aluminium complex is to use it as a fluorescent dopant in OLEDs. The efficiency of the full-color OLED is highly dependent on the deepness of blue emission *i.e.* deeper blue (smaller value of y CIE coordinate) leads to decrease of power consumption in the device.[30] Forrest *et al.* have shown that by using a fluorescent blue emitting dopant along with phosphorescent red and green dopants can considerably increase luminance efficiency in the white light OLED (WOLED) compared with the all-phosphor doped device.[31] Very recently, it has been shown that blue fluorescent binaphthalene derivatives work efficiently as host and light emitting materials in OLEDs without problems faced by blue phosphorescent materials in OLEDs.[30a] Lately, it has also been shown that doping the parent Alq_3 in an UV-emitting polymer matrix increases fluorescence efficiency of the parent Alq_3 caused by resonance energy transfer from the polymer to the parent Alq_3.[32]

3. Experimental section

3.1 Syntheses of quinoline derivatives

3.1.1 Synthesis of 8-(benzyloxy)-4-chloroquinoline (2). 4-Chloro-8-hydroxyquinoline **1** (401 mg, 2.23 mmol) and anhydrous K_2CO_3 (616 mg, 4.46 mmol) were mixed in dimethylformamide (DMF) (4 mL) under argon atmosphere for 10 min. Benzyl bromide (0.30 mL, 2.53 mmol) was added and the reaction mixture was stirred for 18 h at room temperature.

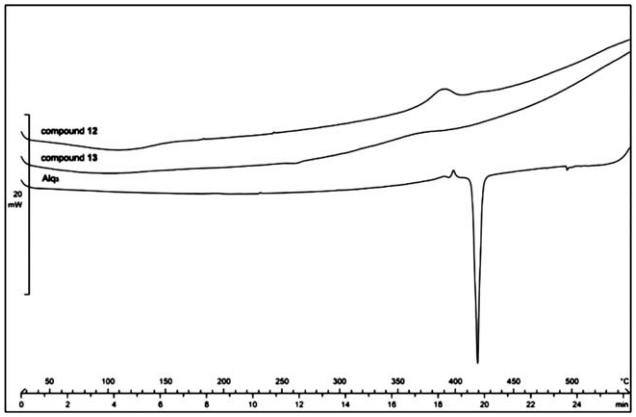


Fig. 6 DSC thermograms of the parent Alq_3 and compounds **12** and **13**.

Solvent was removed by a rotary evaporator. The reaction product was dissolved in acetone, filtered through a silica layer and evaporated to dryness. The desired product was collected after flash chromatography (1 : 1 ethyl acetate/*n*-hexane) as white powder (492 mg, 82%). Mp 133 °C. ^{1}H NMR δ_H (200 MHz; DMSO-d_6; Me_4Si) 5.33 (2H, s, CH_2), 7.32–7.47 (4H, m), 7.53–7.58 (2H, m), 7.63–7.81 (3H, m), 8.79 (1H, d, *J* 4.7). ^{13}C NMR δ_C (50 MHz; DMSO-d_6; Me_4Si) 70.1 (CH_2), 110.9, 115.1, 122.1, 126.7, 127.9 (2C, Ph), 128.4, 128.4 (2C, Ph), 136.7, 140.7, 140.9, 148.8, 154.4. HRMS: calcd for $C_{16}H_{13}NOCl$ ([M + H]$^+$) 270.0686, found 270.0679.

3.1.2 Synthesis of 4-benzyloxy-11*H*-indol[3,2-*c*]quinoline (3). Compound **2** (390 mg, 1.45 mmol) was stirred in 2-bromoaniline (2.60 g, 15.1 mmol) under argon atmosphere for 17 h. The oil bath temperature was adjusted to 135 °C. The reaction mixture was allowed to cool to room temperature. Acetone (6.5 mL) was added and the precipitate was filtered and washed with acetone (35 mL). The crude product was boiled in a mixture of 1 M NaOH (aq) (4.5 mL), acetone (2 mL) and distilled water (8 mL) for 10 min. The mixture was cooled to room temperature. The precipitate was filtered, washed with distilled water and dried at 60 °C overnight. Dimethylacetamide (DMA) (8 mL) was bubbled with argon for 15 min. Dried quinoline derivative[33] (550 mg, 1.36 mmol), $Pd(OAc)_2$ (17.5 mg, 0.069 mmol), PCy_3-HBF_4 (52.0 mg, 0.141 mmol) and anhydrous K_2CO_3 (471 mg, 3.41 mmol) were added to the reaction vessel against the argon flow. The reaction mixture was stirred and heated (oil bath 160 °C) under argon atmosphere for 3 h. The hot reaction mixture was filtered through a silica layer, silica was washed with acetone (50 mL) and the filtrate was evaporated to dryness. The crude product was dissolved in acetone (8 mL) and the solution was added to distilled water (25 mL) dropwise. The precipitate was filtered, washed with distilled water and dried at 60 °C. The procedure gave the pure product as light brown powder (434 mg, 93%). Mp 282 °C. ^{1}H NMR δ_H (200 MHz; DMSO-d_6; Me_4Si) 5.36 (2H, s, CH_2), 7.29–7.63 (10H, m), 7.71 (1H, d, *J* 8.0), 8.07 (1H, d, *J* 7.2), 8.31 (1H, d, *J* 7.8), 9.53 (1H, s), 12.65 (1H, s, NH). ^{13}C NMR δ_C (50 MHz; DMSO-d_6; Me_4Si) 70.1 (CH_2), 109.6, 111.9, 114.0, 114.7, 118.2, 120.2, 120.6, 121.8, 125.7, 126.0, 127.9, 128.0 (2C, Ph), 128.4 (2C, Ph), 137.1, 137.2, 138.9, 139.9, 143.1, 155.0. HRMS: calcd for $C_{22}H_{17}N_2O$ ([M + H]$^+$) 325.1341, found 325.1347.

3.1.3 Synthesis of 11*H*-indolo[3,2-*c*]quinolin-4-ol (4). Compound **3** (600 mg, 1.85 mmol) and 10 wt% Pd–C (122 mg) were refluxed in ethanol (18 mL) under H_2 atmosphere (balloon) for 5 h. The hot reaction mixture was filtered, washed with hot ethanol (35 mL) and the filtrate was evaporated to dryness. The crude product was dissolved in ethanol (15 mL) and added dropwise to distilled water (45 mL). The precipitate was filtered, washed with distilled water and dried at 60 °C. The procedure gave the pure product as yellow powder (409 mg, 94%). Mp 254 °C. ^{1}H NMR δ_H (200 MHz; DMSO-d_6; Me_4Si) 7.09 (1H, dd, *J* 7.7, 1.1), 7.31–7.39 (1H, m), 7.46–7.56 (2H, m), 7.71 (1H, d, *J* 8.0), 7.92 (1H, dd, *J* 8.2, 1.2), 8.34 (1H, d, *J* 7.8), 9.55 (1H, s), 12.69 (1H, s, NH). ^{13}C NMR δ_C (50 MHz; DMSO-d_6; Me_4Si) 110.5, 111.9, 112.0, 114.8, 117.7, 120.3, 120.7, 122.0, 125.7, 126.7, 135.5, 139.0, 140.1, 142.4, 153.9. HRMS: calcd for $C_{15}H_{11}N_2O$ ([M + H]$^+$) 235.0871, found 235.0889.

3.1.4 Synthesis of 4-((2-bromobenzyl)(methyl)amino)quinolin-8-yl 4-methylbenzenesulfonate (5). Compound **1** (503 mg, 2.80 mmol) was stirred in 2-bromo-*N*-methylbenzylamine (3.50 g, 17.5 mmol) under argon atmosphere for 17 h. The oil bath temperature was adjusted to 135 °C. The reaction mixture was allowed to cool to room temperature. Ethyl acetate (5 mL) was added and the solution was extracted with 6% HCl (aq) (25 mL). Separated aqueous layer was allowed to stand at room temperature overnight and for 30 min on an ice bath. The resulting precipitate was filtered and washed with two 5 mL portions of 6% HCl (aq) and distilled water (5 mL). The precipitate was dried at 60 °C. The intermediate product (723 mg, 1.90 mmol)[34] was boiled in 1 M NaOH (aq) (3.80 mL) and distilled water (5 mL) for 15 min. The mixture was allowed to cool to room temperature. *p*-Toluenesulfonyl chloride (363 mg, 1.90 mmol) in acetone (15 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1 h. The mixture was concentrated by evaporation to half. Distilled water (10 mL) was added and the mixture was kept on an ice bath for 10 min. The precipitate was filtered, washed with distilled water and dried at 60 °C. The procedure gave the pure product as light brown powder (697 mg, 50%). Mp 151 °C. ^{1}H NMR δ_H (200 MHz; DMSO-d_6; Me_4Si) 2.38 (3H, s, Me), 2.93 (3H, s, NMe), 4.50 (2H, s, CH_2), 6.98 (1H, d, *J* 5.1), 7.24–7.48 (6H, m), 7.57–7.68 (2H, m), 7.81–7.85 (3H, m), 8.54 (1H, d, *J* 4.9). ^{13}C NMR δ_C (50 MHz; DMSO-d_6; Me_4Si) 21.2 (Me), 59.3 (NMe), 65.6 (CH_2), 109.1, 121.4, 123.0, 123.1, 124.0, 124.1, 128.1, 128.3 (2C, Ph), 129.5, 129.5, 129.8 (2C, Ph), 132.7, 133.0, 136.0, 142.7, 145.3, 145.4, 150.7, 155.9. HRMS: calcd for $C_{24}H_{22}N_2O_3SBr$ ([M + H]$^+$) 497.0535, found 497.0531.

3.1.5 Synthesis of 5-methyl-5,6-dihydrodibenzo[*c*,*h*][1,6]naphthyridin-1-yl 4-methylbenzene-sulfonate (6). DMA (3.75 mL) was bubbled with argon for 15 min. Compound **5** (251 mg, 0.505 mmol), $Pd(OAc)_2$ (13.2 mg, 0.052 mmol), PCy_3-HBF_4 (38.8 mg, 0.105 mmol) and anhydrous K_2CO_3 (184 mg, 1.33 mmol) were added to the reaction vessel against the argon flow. The reaction mixture was stirred and heated (oil bath 160 °C) under argon atmosphere for 4 h. The hot reaction mixture was filtered through a silica layer, silica was washed with acetone (50 mL) and the filtrate was evaporated to dryness. The crude product was boiled in acetone (1 mL) after flash chromatography and *n*-hexane (4 mL) was slowly added. The mixture was cooled to

room temperature and kept on an ice bath for 15 min. The precipitate was filtered, washed with cold solvent mixture (3 mL of acetone and 12 mL of *n*-hexane) and dried at 60 °C. The procedure gave the product as off-white powder (115 mg, 55%). Mp 161 °C. ^{1}H NMR δ_H (200 MHz; DMSO-d_6; Me_4Si) 2.41 (3H, s, Me), 2.99 (3H, s, NMe), 4.37 (2H, s, CH_2), 7.33–7.57 (7H, m), 7.87 (2H, d, *J* 8.2), 8.05–8.09 (1H, m), 8.15 (1H, d, $J = 7.6$), 9.30 (1H, s). ^{13}C NMR δ_C (50 MHz; DMSO-d_6; Me_4Si) 21.2 (Me), 42.6 (NMe), 53.5 (CH_2), 119.6, 121.4, 122.3, 123.6, 124.4, 125.3, 126.7, 128.0, 128.3 (2C, Ph), 128.5, 128.9, 129.9 (2C, Ph), 131.0, 132.7, 141.8, 145.4, 145.5, 147.1, 150.3. HRMS: calcd for $C_{24}H_{20}N_2O_3NaS$ ($[M + Na]^+$) 439.1092, found 439.1104.

3.1.6 Synthesis of 5-methyl-5,6-dihydrodibenzo[*c*,*h*][1,6]naphthyridin-1-ol (7). Compound **6** (221 mg, 0.531 mmol), NaOH (aq) (1 M, 2.65 mL, 2.65 mmol) and ethanol (10 mL) were refluxed for $2^1/_2$ h. Solvents were removed by a rotary evaporator. Distilled water (5 mL) and ethanol (5 mL) were added and the pH was adjusted to 7 with 6% HCl (aq). Distilled water (20 mL) was added and the resulting precipitate was filtered. The solid product was washed with distilled water and dried at 60 °C. The product was collected as greenish powder (117 mg, 84%). Mp 159 °C. ^{1}H NMR δ_H (200 MHz; DMSO-d_6; Me_4Si) 2.97 (3H, s, NMe), 4.35 (2H, s, CH_2), 7.03 (1H, d, *J* 7.43), 7.28–7.53 (4H, m), 7.62 (1H, d, *J* 8.22), 8.08 (1H, d, *J* 6.06), 9.27 (1H, s), 9.69 (1H, br s, OH). ^{13}C NMR δ_C (50 MHz; DMSO-d_6; Me_4Si) 43.5 (NMe), 54.9 (CH_2), 112.3, 115.4, 120.7, 123.5, 124.9, 128.1, 128.1, 129.3, 129.5, 130.7, 132.3, 140.3, 145.5, 152.0, 155.1. HRMS: calcd for $C_{17}H_{15}N_2O$ ($[M + H]^+$) 263.1184, found 263.1181.

3.1.7 Synthesis of 4-(2-bromobenzyloxy)quinolin-8-yl 4-methylbenzenesulfonate (9). NaH in 60% mineral oil (105 mg, 2.63 mmol) was washed with *n*-hexane (2 mL) under argon atmosphere. 4-Hydroxy-8-tosyloxyquinoline **8** (502 mg, 1.59 mmol) in DMF (5 mL) was added and reaction was allowed to proceed for 5 min. 2-Bromobenzyl bromide (615 mg, 2.46 mmol) was added and the reaction solution was mixed for 24 h at room temperature. The reaction mixture was evaporated to dryness. The product was collected as off-white powder (586 mg, 76%) after flash chromatography (1 : 1 ethyl acetate/*n*-hexane). Mp 163 °C. ^{1}H NMR δ_H (200 MHz; DMSO-d_6; Me_4Si) 2.38 (3H, s, Me), 5.40 (2H, s, CH_2), 7.21 (1H, d, *J* 5.3), 7.32–7.57 (6H, m), 7.69–7.75 (2H, m), 7.82 (2H, d, *J* 8.2), 8.09 (1H, dd, *J* 7.7, 2.1), 8.69 (1H, d, $J = 5.3$). ^{13}C NMR δ_C (50 MHz; DMSO-d_6; Me_4Si) 21.2 (Me), 70.0 (CH_2), 102.9, 121.0, 122.3, 122.5, 123.3, 125.5, 128.1, 128.4, 129.9, 130.7, 130.8, 132.5, 132.9, 134.8, 142.0, 144.8, 145.4, 152.2, 160.1. HRMS: calcd for $C_{23}H_{19}NO_4SBr$ ($[M + H]^+$) 484.0218, found 484.0208.

3.1.8 Synthesis of 6*H*-isochromeno[4,3-*c*]quinolin-1-yl 4-methylbenzenesulfonate (10). DMA (6 mL) was bubbled with argon for 15 min. Compound **9** (402 mg, 0.830 mmol), $Pd(OAc)_2$ (10.8 mg, 0.043 mmol), PCy_3-HBF_4 (32.3 mg, 0.088 mmol) and anhydrous K_2CO_3 (287 mg, 2.08 mmol) were added to the reaction vessel against the argon flow. The reaction mixture was stirred and heated (oil bath 160 °C) under argon atmosphere for 3 h. The hot reaction mixture was filtered through a silica layer, silica was washed with acetone (50 mL) and the filtrate was evaporated to dryness. The crude product was boiled in acetone (5 mL) after flash chromatography (1 : 1 ethyl acetate/*n*-hexane) and *n*-hexane (15 mL) was slowly added. The mixture was cooled to room temperature and kept on an ice bath for 15 min. The precipitate was filtered, washed with cold solvent mixture (10 mL of acetone and 30 mL of *n*-hexane) and dried at 60 °C. The procedure gave the product as off-white powder (290 mg, 87%). Mp 200 °C. ^{1}H NMR δ_H (200 MHz; DMSO-d_6; Me_4Si) 2.40 (3H, s, Me), 5.53 (2H, s, CH_2), 7.34–7.61 (7H, m), 7.85 (2H, d, *J* 8.2), 8.04–8.10 (2H, m), 9.32 (1H, s). ^{13}C NMR δ_C (50 MHz; DMSO-d_6; Me_4Si) 21.2 (Me), 68.8 (CH_2), 113.5, 121.1, 121.5, 121.8, 122.4, 125.3, 126.1, 126.7, 128.3, 128.8, 128.9, 129.7, 130.0, 132.4, 141.7, 145.0, 145.5, 147.1, 156.0. HRMS: calcd for $C_{23}H_{18}NO_4S$ ($[M + H]^+$) 404.0957, found 404.0950.

3.1.9 Synthesis of 6*H*-isochromeno[4,3-*c*]quinolin-1-ol (11). Compound **10** (517 mg, 1.28 mmol), NaOH (aq) (1 M, 3.85 mL, 3.85 mmol), ethanol (12.5 mL) and acetone (12.5 mL) were refluxed for $2^1/_2$ h. The solvents were removed by a rotary evaporator. Distilled water (6 mL) was added. pH was adjusted to 6 with 6% HCl (aq). The precipitate was filtered, washed with distilled water and finally dried at 60 °C. The procedure gave the product as off-white powder (319 mg, >99%). Mp 192 °C. ^{1}H NMR δ_H (200 MHz; DMSO-d_6; Me_4Si) 5.49 (2H, s, CH_2), 7.08 (1H, d, *J* 7.4), 7.32–7.57 (5H, m), 8.08 (1H, d, *J* 7.2), 9.29 (1H, s), 9.82 (1H, br s, OH). ^{13}C NMR δ_C (50 MHz; DMSO-d_6; Me_4Si) 68.6 (CH_2), 111.4, 112.1, 113.2, 120.6, 121.7, 125.2, 127.3, 127.4, 128.5, 128.8, 129.7, 139.2, 144.1, 153.5, 156.4. HRMS: calcd for $C_{16}H_{12}NO_2$ ($[M + H]^+$) 250.0868, found 250.0873.

3.2 General procedure for syntheses of Alq_3 derivatives

Ligand (3 equiv), anhydrous K_2CO_3 (3 equiv), and $Al(NO_3)_3 \cdot 9H_2O$ (1 equiv) were refluxed in ethanol for 23 h under argon atmosphere. The reaction mixture was allowed to cool to room temperature. The precipitate was filtered and washed sequentially with ethanol, distilled water and ethanol. The product was dried at 60 °C.

3.2.1 Synthesis of tris-(11*H*-indolo[3,2-*c*]quinolin-4-ol) aluminium (12). The specific amounts of chemicals used: compound **4** (60.2 mg, 0.257 mmol), anhydrous K_2CO_3 (43.0 mg, 311 mmol), $Al(NO_3)_3 \cdot 9H_2O$ (32.3 mg, 0.086 mmol) and ethanol (6 mL). The procedure gave the product as white powder (57.3 mg, 92%). ^{1}H NMR δ_H (200 MHz; DMSO-d_6; Me_4Si) 6.75 (1H, dd, *J* 7.14, 1.27), 6.98–7.04 (2H, m), 7.12 (1H, t, *J* 7.43), 7.28–7.73 (14H, m), 7.84 (1H, d, *J* 8.02), 8.22–8.28 (3H, m), 9.32 (1H, s), 9.55 (1H, s), 12.99 (3H, br s). HRMS: calcd for $C_{45}H_{27}N_6O_3NaAl$ ($[M + Na]^+$) 749.1858, found 749.1842.

3.2.2 Synthesis of tris-(5-methyl-5,6-dihydrodibenzo[*c*,*h*][1,6] naphthyridin-1-ol)aluminium (13). The specific amounts of chemicals used: compound **7** (57.6 mg, 0.220 mmol), anhydrous K_2CO_3 (30.7 mg, 0.222 mmol), $Al(NO_3)_3 \cdot 9H_2O$ (27.5 mg, 0.073 mmol) and ethanol (5.75 mL). The procedure gave the product as beige powder (42.7 mg, 72%). ^{1}H NMR δ_H (200 MHz; $CDCl_3$; Me_4Si) 3.29–3.43 (9H, m, NMe), 4.33–4.46 (6H, m, CH_2), 7.03–7.78 (22H, m), 9.16 (1H, s), 9.26 (1H, s). HRMS: calcd for $C_{51}H_{40}N_6O_3Al$ ($[M + H]^+$) 811.2977, found 811.2981.

3.2.3 Synthesis of tris-(6*H*-isochromeno[4,3-*c*]quinolin-1-ol) aluminium (14). The specific amounts of chemicals used: compound **11** (100 mg, 0.401 mmol), anhydrous K_2CO_3 (55.4 mg, 0.401 mmol), $Al(NO_3)_3 \cdot 9H_2O$ (50.8 mg, 0.135 mmol) and ethanol (10 mL). The procedure gave the product as off-white powder (86.3 mg, 84%). ^{1}H NMR δ_H (200 MHz; $CDCl_3$; Me_4Si) 5.28–5.54 (6H, m), 7.01 (1H, d, *J* 6.80), 7.11–7.50 (18H, m), 7.64–7.69 (2H, m) 7.80 (1H, s), 9.15 (1H, s), 9.28 (1H, s). HRMS: calcd for $C_{48}H_{30}N_3O_6NaAl$ ([M + Na]$^+$) 794.1848, found 794.1868.

3.3 Chemical characterization

^{1}H and ^{13}C NMR spectra were measured by using a Bruker Avance DPX200 instrument. High resolution mass spectra were measured by using a Micromass LCT device. Thermoanalyses were carried out by using a Mettler Toledo DSC821^e apparatus equipped with a TSO800GC1 Gas Control system. The heating rate was 20 °C min^{-1} and the nitrogen flow 50 mL min^{-1}. Melting points are reported from the peaks and the glass transition temperatures as on-set values from the third heating scan to 350 °C after rapid cooling to 25 °C.

3.4 Photophysical measurements

Compound **12** was soluble in ethanol and compounds **13** and **14** in chloroform. These were used as solvents in optical measurements to prevent possible concentration quenching. Reference solutions of the parent Alq_3 (Sigma-Aldrich, 99.99%) were prepared in both solvents. Concentrations were fixed in order to find a wavelength, where the absorbances of compounds **12–14** and that of the parent Alq_3 reference were the same. Thus the fluorescence quantum yield, Φ, can be determined by comparing directly the number of emitted photons (*i.e.* signal intensity, *I*) throughout the measured spectrum ($I \propto N_{abs} \propto 1 - T = 1 - 10^{-Abs.}$). The relative fluorescence quantum yield, $\Phi = 1.0$, was given to the parent Alq_3 and the fused Alq_3 derivatives (compounds **12–14**) were referenced to that. Sample solutions were kept in a 1 × 1 cm quartz cuvette during the experiments. Absorption and emission spectra were measured by using standard spectrophotometers (Shimadzu UV-3600 UV-vis, Fluorolog Jobin Yvon-SPEX). In each fluorescence measurement, 90° configuration was used for detection.

Films were deposited onto 12 × 36 mm quartz plates by using a programmable spin-coater (WS-400B-6NPP/LITE, Laurell Technologies Corp., 10–10 000 rpm). Concentrations of the solutions (compound **12** in ethanol and compounds **13** and **14** in chloroform) before casting were 0.1 mM and 1 mM in two distinct sets. The spinning speed was 2000 rpm and the time 1 min. Substrates were cleaned prior to deposition by sonicating 1 h in $CHCl_3$ and 1 h in sulfochromic acid followed by rinsing with MilliQ water (Millipore, resistivity >18.0 MΩ cm) and drying in vacuum at 110 °C for 1 h. A test was made to deposit a film by using thermal evaporation in a high vacuum (Edwards AUTO 306). Compounds **12–14** were placed into a ceramic jar (5 mg) and the temperature was increased from 180 to 400 °C, but the layer growth was not observed. A thin film of the parent Alq_3 (9.5 nm) was produced by using thermal evaporation in a high vacuum (2–3 × 10^{-6} mbar) at 200 °C. Additional N_2 plasma treatment (Harrick, 10 min) was applied for the plates, onto which compound **12** was deposited in order to hydrophilize the surface. In fluorescence measurements, the plates were aligned to an angle (45–60°) with respect to the excitation, which yielded the maximum signal intensity.

Fluorescence lifetimes (τ) were obtained by using a time correlated single photon counting (TCSPC) system (Piqoquant GmBH) consisting of a Picoharp 300 controller and a PDL 800-B driver. Pulsed LED (340 nm, 2.5–10 MHz) was used for excitation and a microchannel plate photomultiplier (Hamamatsu R3809U-50) for detection in 90° configuration. Time resolution of a TCSPC measurement is about 300 ps estimated from the FWHM of the instrumental response at 340 nm. Decay associated spectra (DAS) were measured by accumulating the signal for 1 min at each monitoring wavelength (10 nm steps). Pre-exponential amplitudes (*A*) and corresponding lifetimes (τ) were obtained by using an ordinary exponential fitting procedure. Well-known models were used in the analysis.[22] Equations and fluorescence decay data together with DAS are shown in the ESI†. Absolute absorption and emission spectra are shown in the ESI† together with the decay curves, decay associated spectra and calculation procedures.

4. Conclusion

Three new tetracyclic 8-hydroxyquinoline derivatives were synthesized. Readily available 4-chloro-8-hydroxyquinoline **1** and 4-hydroxy-8-tosyloxyquinoline **8** were applied as starting materials in the syntheses. Aminations were performed by using solvent free amination reactions. The hydroxyl group at the 8-position of the quinoline ring was protected with the tosyl or benzyl group prior to intramolecular direct arylation reactions. Direct arylation reactions were carried out efficiently by using Pd$(OAc)_2$ as a palladium source and air stable PCy_3-HBF_4 as a ligand. Deprotection of the benzyl group or the tosyl group gave the desired ligands in good to quantitative yields. Finally, aluminium complexes were prepared from the synthesized ligands and the spectroscopic properties of the complexes were studied in detail both in solution and solid state.

All new tetracyclic Alq_3 derivatives have blue-shifted absorption maximum and show increased molar extinction coefficients compared with the parent Alq_3. A strong EDG on the 4-position of the quinoline ring seems to affect the absorption profile more than the extended conjugation sphere. Derivatives have also blue-shifted emission and decreased Stokes' shifts compared with the parent Alq_3. Evidently, decreased Stokes' shifts are related to rigid tetracyclic structures. Especially interesting observation is that the aluminium complex of 11*H*-indolo[3,2-*c*]quinolin-4-ol **12** has 3.1–3.5 times higher fluorescence quantum yield than the parent Alq_3 and the most blue-shifted emission maximum among the Alq_3 derivatives to date and CIE chromaticity coordinates locating on the deep blue area (0.16, 0.12). Moreover, spectroscopic properties of compound **12** did not show major differences between the solution and the solid states. Obviously in the case of tris-(5-methyl-5,6-dihydrodibenzo[*c*,*h*][1,6]naphthyridin-1-ol)aluminium **13**, charge transfer is taking place in the molecule which explains partly that only the small blue-shift of emission occurs and a consequent TICT state is likely to cause the observed second decay of fluorescence. Compound **13** also has dramatically decreased

the fluorescence quantum yield compared with the parent Alq_3. In addition, emission could not be detected in the solid state. Tris-(6*H*-isochromeno[4,3-*c*]quinolin-1-ol)aluminium **14** has similar blue-shifted absorption and emission like its unfused analogue tris-(4-benzyloxy-8-hydroxyquinoline)aluminium[6a] but the fluorescence quantum yield is considerably higher which can be explained by the rigid fused structure of the ligands. Compound **14** shows pronounced emission broadening in the solid state, which is attributed to the crystalline nature of the compound in the solid state. DSC analyses indicate that compounds **12** and **13** are amorphous whereas compound **14** and the parent Alq_3 have sharp melting endotherms. Based on the results, 11*H*-indolo[3,2-*c*]quinolin-4-ol **4** has especially promising features to be applied as a ligand for aluminium or other metal ions in different applications.

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