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## COMMUNICATION

## Triarylboron-functionalized 8-hydroxyquinolines and their aluminium(III) complexes<sup>†</sup>

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The first examples of triarylboron-functionalized 8-hydroxyquinoline ligands and their aluminium complexes have been synthesized. These luminescent derivatives of the well-known electron transport material tris(8-hydroxyquinoline)aluminium (Alq<sub>3</sub>) display enhanced electron-accepting ability relative to Alq<sub>3</sub>, and can also be used as an indicator for small  $F^-$  and  $CN^$ anions.

The discovery of electroluminescence from thin films of tris(8-hydroxyquinoline)aluminium (Alq<sub>3</sub>) in 1987 has since led to a vast body of research into the design and fabrication of organic light emitting diodes (OLEDs).<sup>1</sup> This new technology allows for the fabrication of efficient and durable displays with high contrast that can be printed on wafer-thin substrates, and is likely to bring profound changes to the display industry in the years to come. Alq<sub>3</sub> in particular is best known for its electron transporting characteristics, and in this capacity has been studied extensively for use in OLEDs.<sup>1,2</sup> Due to a substantial body of research and a better understanding of the electronic characteristics of this material, many derivatives now exist with well-controlled photophysical properties.<sup>3e,f,4,5</sup>

Nonetheless, electron transport materials (ETMs) for OLEDs are in general less effective at transporting charge than hole transport materials (HTMs). Electron mobilities in organic materials are typically 1–2 orders of magnitude lower than hole mobilities,<sup>6</sup> often leading to reduced device efficiency and lifetime due to poor carrier balance and an accumulation of positive charge.<sup>7</sup> As such, the development of improved electron-transport materials remains a subject of considerable research effort.

Triarylboron compounds have also been studied as electron-transport materials due to the empty low-lying  $p_{\pi}$  orbital on the boron center, which allows them to act as excellent electron acceptors. In addition, this functionality contributes unique luminescent properties to their respective chromophores, often promoting intense charge-transfer luminescence.<sup>8</sup> Furthermore, sterically protected dimesitylboron compounds can be used as selective chemical indicators

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due to the susceptibility of the empty  $p_{\pi}$ -orbital to attack from small nucleophiles, giving accompanying changes in its absorption or emission profile.<sup>9</sup> Although Bpin-functionalized Alq<sub>3</sub> is known previously,<sup>5g,h</sup> triarylboron derivatives of Alq<sub>3</sub> have not been reported in literature. The addition of a dimesitylboron moiety to Alq<sub>3</sub> could thus result in a multifunctional complex capable of acting as an emissive or electron-transport material in OLEDs, as well as an indicator for small nucleophilic anions. To this end, we herein report the synthesis and photophysical properties of the first examples of 8-hydroxyquinoline ligands functionalized with triarylboron and their aluminium complexes.

Ligands 1 and 2 were designed with rigid and flexible linkers between the hydroxyquinoline and boron moieties, respectively. Both of these linkers should promote electronic communication, with compound 1 possessing a highly planar acetylene  $\pi$  system, and compound 2 incorporating a hexylthiophene linker that is widely used to facilitate electron transfer in optoelectronic materials.<sup>8a,10</sup> The synthetic route to each ligand is presented in Scheme 1. Free ligands were only weakly fluorescent at room temperature in solid state and solution ( $\lambda_{max} = 413$  nm for 1, 480 nm for 2) due to the presence of the phenolic proton, which can quench fluorescent emission by excited-state proton transfer.<sup>11</sup> As this functional group is also capable of hydrogen bonding, the response of



Scheme 1 Reagents and conditions: (i) n-BuLi, THF, -78 °C; (ii) FBMes<sub>2</sub>, THF, -78 to 25 °C; (iii) CuI, DIPEA, Pd(PPh<sub>3</sub>)<sub>4</sub>, THF, 25 °C; (iv) piperidine, CH<sub>2</sub>Cl<sub>2</sub>, 25 °C; (v) B(pin)(O<sup>i</sup>Pr), THF, -78 to 25 °C; (vi) Pd(OAc)<sub>2</sub>, SPhos, K<sub>3</sub>PO<sub>4</sub>, toluene, reflux; (vii) HCl, CH<sub>3</sub>OH, reflux.

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these ligands to  $F^-$  and  $CN^-$  was also complex in emission mode (see ESI<sup> $\dagger$ </sup>).

The Al(III) complexes of these ligands, Al(1)<sub>3</sub> and Al(2)<sub>3</sub> (Chart 1) were synthesized by reacting trimethylaluminium with three equivalents of ligand in dry toluene. Consistent with previous observations that *mer*-Alq<sub>3</sub> is the dominating isomer in solution with a  $C_1$  symmetry,<sup>12</sup> both new Al(III) compounds were found to exist as the *mer*-isomer, as evidenced by the three distinct sets of peaks of the 2-, 3- and 4-positions of the quinoline ring in the <sup>1</sup>H NMR spectra (see ESI<sup>†</sup>).

The absorption and emission spectra of these compounds are shown in Fig. 1, alongside those of Alq<sub>3</sub> for comparison. Due to the extended  $\pi$  conjugation and the presence of the boron moiety, both new Al(III) complexes display considerably stronger absorptions over a broader wavelength range than the parent chromophore. Alq<sub>3</sub>, Al(1)<sub>3</sub> and Al(2)<sub>3</sub> show green, yellow and orange fluorescence, respectively, in solid state and solution (Fig. 1, Table 1).

The red shift seen in both new complexes is likely due to extension of the  $\pi$ -skeleton as well as addition of an overall electron donating group to the C-5 position of the quinoline moiety, which is known to cause a bathochromic shift.<sup>4a,5e</sup> In addition, the low-lying p orbital on the boron center will lower the LUMO level of the complex.<sup>8g</sup> This was supported by DFT calculation results at the B3LYP/6-31G\* level of theory, which indicate that the boron centre makes a large contribution to the LUMO level of both new complexes. In addition, the HOMO and LUMO orbitals contain substantial electron density on the phenoxide and pyridyl rings, respectively (see ESI<sup>†</sup>), as is the case for Alq<sub>3</sub>.<sup>3</sup> The emission quantum efficiencies of  $Al(1)_3$  and  $Al(2)_3$  are lower than that of  $Alg_3$ , attributable to the substitution effect at the C5 position of the quinoline.<sup>5,8</sup> The relatively low quantum yield of  $Al(2)_3$  is likely due to the presence of the hexyl chains that reduce the rigidity of the compound and increase the rate of nonradiative decay from the excited state by vibronic coupling. Compared to Alq<sub>3</sub>, the new boron-functionalized complexes  $Al(1)_3$  and  $Al(2)_3$  showed positive shifts in their first reduction potentials, with values of -2.11 and -2.22 V, respectively (relative to  $FeCp_2^{0/+}$ ), supporting improved electron-accepting ability.

Interestingly, both new aluminium complexes display three distinct reduction peaks, suggesting that interactions may exist between the ligands, making successive reductions more difficult than the first.<sup>14</sup> DFT calculations further suggest that the three lowest unoccupied molecular orbitals of both Al(1)<sub>3</sub>





**Fig. 1** Absorption and normalized emission spectra of Alq<sub>3</sub>, Al(1)<sub>3</sub> and Al(2)<sub>3</sub>. Inset: photographs of Alq<sub>3</sub>, Al(1)<sub>3</sub> and Al(2)<sub>3</sub> films and CH<sub>2</sub>Cl<sub>2</sub> solutions (10–5 M) under UV irradiation.



**Fig. 2** The fluorescent titration spectra of Al(1)<sub>3</sub> (left,  $\lambda_{ex} = 420$  nm) and Al(2)<sub>3</sub> (right,  $\lambda_{ex} = 395$  nm) by NEt<sub>4</sub>CN in CH<sub>2</sub>Cl<sub>2</sub> (1.0 × 10<sup>-5</sup> M) at 298 K.

and Al(2)<sub>3</sub> are each based on the p orbital of one boron center and the  $\pi^*$ -orbital of the attached quinoline ring. Due to the *mer* geometry of the complexes, however, the three LUMO levels are nondegenerate. It is interesting that a similar effect is not observed for Alq<sub>3</sub>, which displays only a single reduction peak, suggesting that successive reduction of the complex is not favoured in the absence of the boron centers.

The Lewis acidity of triarylboranes not only allows these compounds to act as electron acceptors, but as receptors for small anions as well.9 We therefore tested the ability of both  $Al(1)_3$  and  $Al(2)_3$  to act as indicators for fluoride and cyanide, using tetrabutylammonium fluoride (TBAF) and tetraethylammonium cyanide (TEACN) as titrants (Fig. 2). In absorption mode, both complexes show quenching of the strong absorption band at  $\sim 375$  nm, that arises from a triarylboron-based charge-transfer from the filled  $\pi$ -orbitals of the mesityl groups to the boron centre as confirmed by DFT calculations. As well, both complexes exhibit partial quenching of the low-energy band at  $\sim$  430 nm, representing the quinoline-based HOMO-LUMO charge-transfer transition which has some contribution from the boron atom as well, based on DFT results. In fluorescence mode, the emission of both compounds is quenched significantly by the addition of either anion.

Since blocking of the boron centre alone is not sufficient cause for this loss of emission, as  $Alq_3$  itself is highly emissive in the absence of the boron centre entirely, the emission quenching by  $CN^-$  for the two complexes is likely caused by

Compound	$\lambda_{abs}/nm \ (\log \epsilon/M^{-1} \ cm^{-1})$	$\lambda_{\rm em}{}^a/{\rm nm}$	$\Phi$ Soln. <sup>b</sup> /solid <sup>c</sup>	$E_{1/2}^{\operatorname{red} d}/\mathrm{V}$	HOMO <sup>e</sup> /eV	LUMO/eV
Alg <sub>3</sub>	260 (5.15), 393 (3.93)	507	0.12/0.14	-2.40	-5.24	-2.40
$Al(1)_3$	266 (5.17), 370 (5.05), 427 (4.73)	533	0.10/0.06	-2.11	-5.21	-2.68
Al(2) <sub>3</sub>	270 (4.99), 337 (4.78), 373 (4.75), 430 (4.44)	570	0.01/0.02	-2.22	-5.13	-2.60
<sup>a</sup> In CH <sub>2</sub> Cl <sub>2</sub> a	t 1 $\times$ 10 <sup>-5</sup> M. <sup>b</sup> Relative to Alq <sub>3</sub> = 0.12. <sup>13 c</sup> M	easured using	g an integration sph	ere. <sup>d</sup> Measured	in DMF relative	to $\operatorname{FeCp}_2^{0/+}$ .

 Table 1
 Photophysical properties of Alq<sub>3</sub> and its derivatives

<sup>e</sup> Determined from the reduction potential and the optical energy gap.

the presence of highly efficient thermal relaxation pathways. Both new complexes exhibit a similar response to both fluoride and cyanide, and the retention of the low-energy quinolinebased charge-transfer band promoted by aluminium chelation suggests that the ligands are not displaced by either anion. However, <sup>1</sup>H NMR titrations of Alq<sub>3</sub> as well as its boronfunctionalized derivatives by the anions suggest that partial ligand replacement by excess fluoride ions may be occurring, while cyanides do not displace the quinoline ligand at all (see ESI<sup>†</sup>). In addition, <sup>11</sup>B NMR showed the characteristic broad three-coordinate boron signal at 40.0 ppm for  $Al(1)_3$ , and a sharp four-coordinate boron signal at -13.6 ppm following the addition of cyanide. This is consistent with the stronger binding to the aluminium centre expected for fluoride over cyanide.

In summary, the first examples of multifunctional triarylboron-containing Alq<sub>3</sub> complexes have been achieved. New ligands were designed with a focus on increasing the electron transport efficiency of the aluminium complexes while retaining the luminescent functionality of the parent chromophore. Cyclic voltammetry measurements indicated that both  $Al(1)_3$  and  $Al(2)_3$  are stronger electron acceptors than  $Alq_3$ , making these complexes promising for use as electrontransport materials in OLEDs. In addition, both complexes demonstrated an ability to act as an indicator for anions, especially cyanide, which quench the luminescence of the sample in both cases. Future work will continue to examine boron-functionalized Alq3 derivatives, and the evaluation of these materials as electron-transport layers in OLEDs is currently underway in our laboratory.

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