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Fluorinated Alq_3 derivatives with tunable optical properties†

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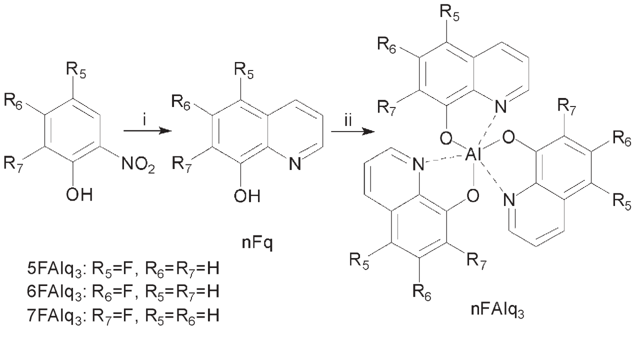
This communication reports that not only the emission colour but also the photoluminescence quantum yield of Alq_3 can be tuned by introducing fluorine atoms at different positions; with fluorination at C-5 the emission is red-shifted with a tremendously decreased intensity, fluorination at C-6 causes a blue-shift with a significantly increased intensity, and fluorination at C-7 has a minor effect on both the colour and intensity of Alq_3's emission.

Since Tang and VanSlyke developed efficient multi-layered organic light-emitting diodes (OLEDs) using tris-(8-hydroxyquinoline) aluminium (**Alq_3**) as the emission and electron transport material,[1] substantial progress has been made in the field, leading to more and more commercial OLED products (cell phones, mp3 players, *etc.*). **Alq_3** is still one of the widely-used fundamental materials in this area due to its excellent thermal stability, high fluorescence efficiency and relatively good electron mobility.[2] Because the efficiency and lifetime of current blue OLEDs are not satisfactory, a lot of researchers are focusing on the molecular tailoring and growth of a new crystalline phase of **Alq_3** in order to shift its emission from the green to the blue region.[3] On the other hand, the F atom is a strong electron-withdrawing group, while fluorinated organic semiconductors possess a high electron mobility, excellent air-stability, low sublimation temperature and perhaps a broadened energy gap.[4] It is supposed that high performance blue OLEDs could be realized from fluorinated **Alq_3** derivatives. Unfortunately, related reports on fluorinated **Alq_3** derivatives are rare so far.[5] In this communication, we have prepared three **Alq_3** derivatives with F atoms at different positions and studied their optical properties systematically. The possible mechanism of the effect of the fluorination position on the optical properties is also discussed.

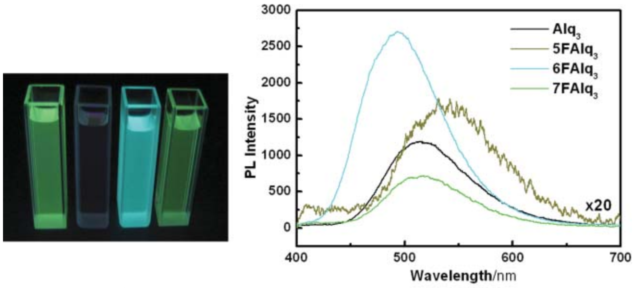
The three ligands of *n*-fluoro-8-hydroxyquinoline (***n*Fq**, $n = 5, 6, 7$) and their complexes of tris-(*n*-fluoro-8-hydroxyquinoline) aluminium (**$nFAlq_3$**, $n = 5, 6, 7$) were synthesized by the synthetic route shown in Scheme 1.‡[6] All **Alq_3** derivatives were purified twice by train sublimation. Through NMR characterization, it is demonstrated that **Alq_3** and its fluorinated derivatives are all obtained as meridianal isomers (refer to the ESI†).



Scheme 1 Synthetic route to fluorinated **Alq_3** derivatives. Reagents and conditions: (i) glycerol, H_2SO_4, reflux 6 h, ∼20%; (ii) toluene, aluminium *iso*-propoxide, reflux 2 h, ∼90%.

Fig. 1 shows the emission and photoluminescence spectra of the three fluorinated **Alq_3** derivatives and their unsubstituted parent compound **Alq_3** in $CHCl_3$ solutions. It is found that **$5FAlq_3$** emits quite weak yellowish-green light (547 nm), while **$6FAlq_3$** emits very strong blueish-green light (495 nm). **$7FAlq_3$** exhibits the same green fluorescence (515 nm) as **Alq_3**, but the intensity decreases to some extent.

The thin films of fluorinated **Alq_3** derivatives show similar tendencies in their spectral characteristics. As seen from Fig. 2, the emission peak of **$5FAlq_3$** is red-shifted by ∼22 nm to 550 nm, with tremendously decreased intensity when compared to that of **Alq_3**. The emission peak of **$6FAlq_3$** is blue-shifted by ∼23 nm to 505 nm with significantly increased intensity. However, both the position



(a) (b)

Fig. 1 (a) Emission of **Alq_3**, **$5FAlq_3$**, **$6FAlq_3$** and **$7FAlq_3$** in $CHCl_3$ solutions (∼1×10^{-5} M, from left to right) upon illumination with UV light (365 nm); (b) Photoluminescence spectra of **Alq_3**, **$5FAlq_3$**, **$6FAlq_3$** and **$7FAlq_3$** in $CHCl_3$ solutions (∼1×10^{-5} M). The excitation wavelength is 370 nm.

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† Electronic supplementary information (ESI) available: UV–vis absorption spectra, ^1H NMR spectra, cyclic voltammograms and further experimental details. See DOI: 10.1039/b516757d

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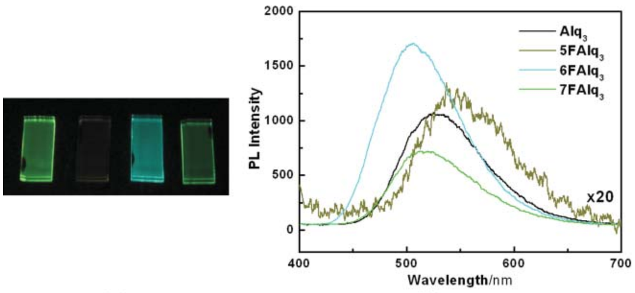

(a) (b)

Fig. 2 (a) Emission of **Alq$_3$**, **5FAlq$_3$**, **6FAlq$_3$** and **7FAlq$_3$** thin films vacuum-deposited on quartz substrates (~50 nm thick, from left to right) upon illumination with UV light (365 nm); (b) Photoluminescence spectra of **Alq$_3$**, **5FAlq$_3$**, **6FAlq$_3$** and **7FAlq$_3$** thin films vacuum-deposited on quartz substrates (~50 nm thick). The excitation wavelength is 370 nm.

and the intensity of the emission peak of **7FAlq$_3$** are similar as those of **Alq$_3$**. The optical data for the fluorinated **Alq$_3$** derivatives are summarized in Table 1. All of these observations indicate that the fluorination position affects greatly the spectral properties.

It has been reported that the light emission of **Alq$_3$** originates from the ligand's electronic π–π* transition from a highest occupied molecular orbital (HOMO) lying mainly on the phenoxide ring to a lowest unoccupied molecular orbital (LUMO) located on the pyridyl ring, which was derived from a molecular simulation of the electronic structure of **Alq$_3$**.[7] Generally speaking, the highest electron density of **Alq$_3$**'s HOMO is located on the phenoxide oxygen and the C-5, C-7 and C-8 positions. Therefore, it is predicted that an electron-withdrawing or electron-donating group at these positions will lead to a blue-shift or red-shift in the absorption and fluorescence spectra. Some reports support this anticipation, for example, by attaching an acceptor group of –CN or a donor group of –CH$_3$ at the C-5 position causes a blue-shift and red-shift, respectively.[7,8] However, this prediction is not suitable in our cases, where the absorption and emission of **5FAlq$_3$** are red-shifted while that of **7FAlq$_3$** is almost unchanged.

To understand what happens in the fluorinated **Alq$_3$** derivatives, we also undertook MO calculations using time-dependent density functional theory (TD-DFT) with 6-31 G(d) basis sets and the Becke three-parameter hybrid exchange-correlation functional (known as B3LYP) to model the HOMOs and LUMOs of these compounds. The calculated HOMOs are shown in Fig. 3. From Fig. 3, it is found that, owing to high electron density at the C-5 position and the lone electron pair on the F atom, the F group takes part in forming the HOMO of **Alq$_3$** through a conjugation effect, giving rise to the higher HOMO energy level of **5FAlq$_3$**. However, the F group at the C-6 position of **6FAlq$_3$** mainly exhibits an electron-withdrawing inductive effect to lower the HOMO energy level, due to the very low electron density at the C-6 position. Therefore, the red-shift or blue-shift of the absorption and emission of **5FAlq$_3$** or **6FAlq$_3$** can be caused by the narrowed or enlarged HOMO–LUMO energy gap of the two compounds, respectively. The hypothesis is supported by their HOMO and LUMO energy levels, obtained from cyclic voltammetry, and their onsets of absorption in solution (see the ESI†). The HOMO–LUMO energy gaps for **5FAlq$_3$** and **6FAlq$_3$** are estimated to be 2.66 and 2.93 eV, respectively; 0.15 eV smaller and 0.12 eV larger than that (2.81 eV) of their parent compound **Alq$_3$**.

Table 1 Photophysical data of the fluorinated **Alq$_3$** derivatives

	Alq$_3$	**5FAlq$_3$**	**6FAlq$_3$**	**7FAlq$_3$**
CHCl$_3$ solution absorption λ_{max}/nm	387	407	375	388
50 nm thick film absorption λ_{max}/nm	392	407	376	388
CHCl$_3$ solution emission λ_{max}/nm	515	547	495	515
50 nm thick film emission λ_{max}/nm	528	550	505	518
PL quantum yield in CHCl$_3$ solution[a]	1.00	0.051	2.62	0.70
PL quantum yield of a 50 nm thick film[a]	1.00	0.091	1.46	0.72

[a] For clarity, the photoluminescence (PL) quantum yield (Φ_{PL}) of all compounds is normalized to Φ_{PL}(**Alq$_3$**) = 1.00.

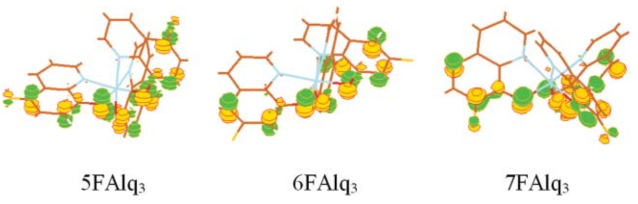

Fig. 3 The location of the highest occupied molecular orbitals (HOMOs) of fluorinated **Alq$_3$** derivatives obtained by MO calculations.

As far as **7FAlq$_3$** is concerned, the F group at the C-7 position also has a conjugation effect, but the energy gap and the emission of **7FAlq$_3$** are similar to those of **Alq$_3$**. We speculate that the steric hindrance and electrostatic repulsion between the 7-F and 8-O atoms in **7FAlq$_3$** may weaken the conjugation effect between the F group and the phenoxide ring, meaning that fluorination has little influence on the energy gap and the emission of **Alq$_3$**.

It is interesting to notice from Table 1 that fluorination also has a great effect on the photoluminescence quantum yield of the fluorinated **Alq$_3$** derivatives. Sapochak *et al.* suggested that the stronger coupling of the metal–ligand stretching coordinating to the electronic transition in **Alq$_3$** may provide additional paths for non-radioactive decay.[8] Therefore, the tremendous decrease in the photoluminescence quantum yield (Φ_{PL}) of **5FAlq$_3$** is reasonable because the conjugation effect makes the coupling of the metal–ligand stretching stronger and increases the energy loss in the excited state vibration. On the other hand, the great enhancement in the Φ_{PL} of **6FAlq$_3$** is due to the reduced energy loss in the excited state vibration.

In a summary, the emission colour of **Alq$_3$** can be tuned towards the direction of blue light by introducing a F atom in an appropriate position (**6FAlq$_3$**). In the meantime, the photoluminescence quantum yield can also be enhanced significantly. This provides us with a new approach to the design and preparation of high-performance luminescence materials for blue OLEDs, for example, by introducing a strong electron-withdrawing group at C-6 of the phenoxide ring together with an electron-donating group at C-4 of the pyridyl ring in **Alq$_3$**. Work along these lines is now in progress.

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Notes and references

‡ ^{1}H NMR spectroscopic and elemental analyses: **5Fq** δ_H (500 MHz, CDCl$_3$): 8.81–8.83 (q, 1 H), 8.39–8.41 (q, 1 H), 7.49–7.51 (q, 1 H) and 7.05–7.15 (m, 2 H); **6Fq** δ_H: 8.72–8.73 (q, 1 H), 8.10–8.12 (q, 1 H), 7.45–7.48 (q, 1 H) and 6.95–6.99 (m, 2 H); **7Fq** δ_H: 8.81–8.82 (q, 1 H), 8.15–8.17 (q, 1 H),

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7.37–7.43 (m, 2 H) and 7.30–7.33 (q, 1 H). Calc. for C_9H_6NOF: C, 66.26; H, 3.71; N, 8.59. Found: **5Fq**: C, 66.15; H, 3.75; N, 8.68. **6Fq**: C, 66.51; H, 3.69; N, 8.36. **7Fq**: C, 66.15; H, 3.64; N, 8.49%.

Calc. for $Al(C_9H_5NOF)_3$: C, 63.17; H, 2.94; N, 8.18. Found: **5FAlq$_3$**: C, 63.21; H, 3.06; N, 8.02. **6FAlq$_3$**: C, 63.47; H, 2.88; N, 7.97. **7FAlq$_3$**: C, 63.61; H, 2.83; N, 7.68%.

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