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ORIGINAL ARTICLE

Study on Relationship Between Fluorescence Properties and Structure of Substituted 8-Hydroxyquinoline Zinc Complexes

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Abstract
Organic light-emitting diodes (OLEDs) produced from 8-hydroxyquinoline metal complexes play a vital role in modern electroluminescent devices. In this manuscript, a series of 8-hydroxyquinoline derivatives were synthesized by different methods and their corresponding zinc metal complexes were prepared. The UV and fluorescence properties of the complexes were measured aiming to understand the effect of substituents at the quinoline ring on the fluorescence properties of the complexes. When the C-5 of 8-hydroxyquinoline was replaced by halogen group, the fluorescence emission wavelengths had been red-shifted, at the same time, blue-shifted of fluorescence emission wavelength was observed when the C-5 position of 8-hydroxyquinoline was substituted by electron-withdrawing group. When the C-4 position of 8-hydroxyquinolie was substituted by methyl or the C-5 position was substituted by sulfonic acid group, the corresponding zinc complexes had higher fluorescence intensity than 8-hydroxyquinolie zinc.

Keywords 8-hydroxyquinoline derivatives · Fluorescence · Substituents · Zinc

Introduction

Organic light-emitting diodes (OLEDs) are booming right now: after the launch of commercial OLED displays based on 8-hydroxyquinoline metal complexes, OLEDs are on their way to replace LCD technology [1–3]. The studies on synthesis and performances of 8-hydroxyquinoline derivative ligands and their different metal complexes have been widely focused [4–7]. 8-hydroxyquinoline or its derivatives combine with metal ions, such as Zn [8], Cd [9], Yb [10], Cu [11], Al [12], and so on, can obtain different luminescent materials with the properties of photoluminescence efficiency, quantum yield, stability, light emission color, etc.

Despite several endeavors surrounding 8-hydroxyquinoline derivatives and their metal complexes, the influence of different substituents of 8-hydroxyquinoline metal complexes about fluorescence properties were rarely reported. In the present, a combined experimental and theoretical method was used to investigate the influence of substituents of quinoline ring on the fluorescence properties of the complexes.

Experimental

The synthesis and characterization data of ligands were showed in the supporting material.

General procedure of complex preparation

The 8-hydroxyquinoline derivative ligands were added to anhydrous methanol at room temperature then the temperature was raised to 70 °C. After the mixture temperature reached 70 °C, an aqueous solution of zinc chloride (2: 1 ratio of the ligand to the metal salt solution) was slowly added drop-wise, and the mixture was refluxed at 70 °C for 20 h. The pH of the mixture was adjusted with ammonia solution to about 7, followed by reaction for 4 h, allowed to stand and suction

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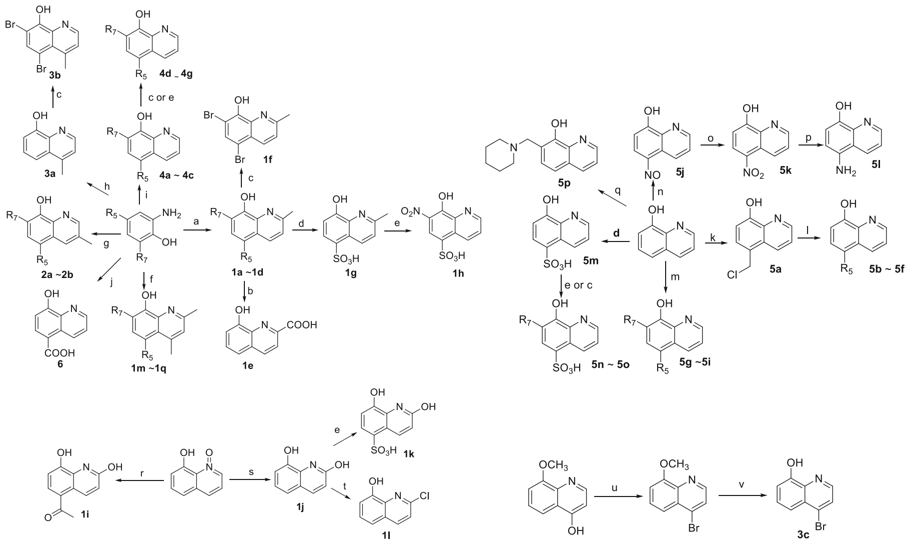


Scheme 1 Preparation of 8-hydroxyquinoline derivatives (a): HCl, crotonaldehyde, 90 °C, 5 h; (b): SeO$_2$, 90 °C, 16 h; (c): bromine rt.; (d): concentrated sulfuric acid, 0-5 °C, 30 h; (e): sulfuric acid, KNO$_3$, 10 °C, 8 h; (f): HCl, 3-penten-2-one, 90 °C, 5 h; (g): HCl, methacryladehyde, 90 °C, 5 h; (h): HCl, but-3-en-2-one, 90 °C, 3 h; (i): sulfuric acid, 2-amino-4-methylphenol derivatives, glycerol, 90 °C, 15 min;. (j): HCl, acrolein, 90 °C, 3 h. (k): 37%formaldehyde, hydrochloric acid; (l) aqueous ammonia; CH$_3$ONa, CH$_3$OH; KHCO$_3$, ethanol; ammonia; dimethylamine, triethylamine; piperidine, chloroform; morpholine, chloroform; (m): *p*-toluidine, NaNO$_2$; bromine; Sodium chlorite, sodium iodide; (n): NaNO$_2$, sulfuric acid; (o) sulfuric acid, HNO$_3$; (p) stannous chloride, HCl (aq), 80 °C; (q): paraformaldehyde, piperidine, ethanol, reflux, 5 h; (r): acetic anhydride, acetyl chloride, ice bath, 5 h; (s): acetic anhydride, potassium carbonate, methanol, RT, 1 h; (t): POCl$_3$, HCl; (u) POBr$_3$, reflux,1.5 h; (v): HBr, reflux

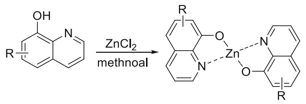
filtered to obtain a cake, which was recrystallized from anhydrous methanol to give the product.

Fluorescence Measurement

For preparation of fluorescence measurement, the metal complexes were dissolved in methanol at 2×10^{-5} mol/L. All fluorescence spectra were recorded on a FL-4600 fluorescence spectrometer using a 1 cm path length quartz cuvette. The fluorescence spectra was recorded from 200 to 600 nm. Both the widths of excitation and emission slits were set at 5.0 nm and the scanning speed was set at 1200 nm·min^{-1}. The maximum excitation wavelengths (λex) and the maximum emission wavelengths (λem) for all metal complexes were tested, respectively. All measurements were conducted at room temperature. The fluorescence data of all metal complexes were showed in the supporting material.

Results and discussion

In the present, a series of 8-hydroxyquinoline derivatives were synthesized through different methods (Scheme 1) and the corresponding zinc metal complexes (Scheme 2) were prepared. The structures of ligands were presented in Fig. 1. Simultaneously, the fluorescence properties of these metal complexes were discussed in detail. The experimental results demonstrated that different substituents on quinoline ring had diverse influence on the fluorescence properties.



Scheme 2 Preparation of 8-hydroxyquinoline zinc complexes

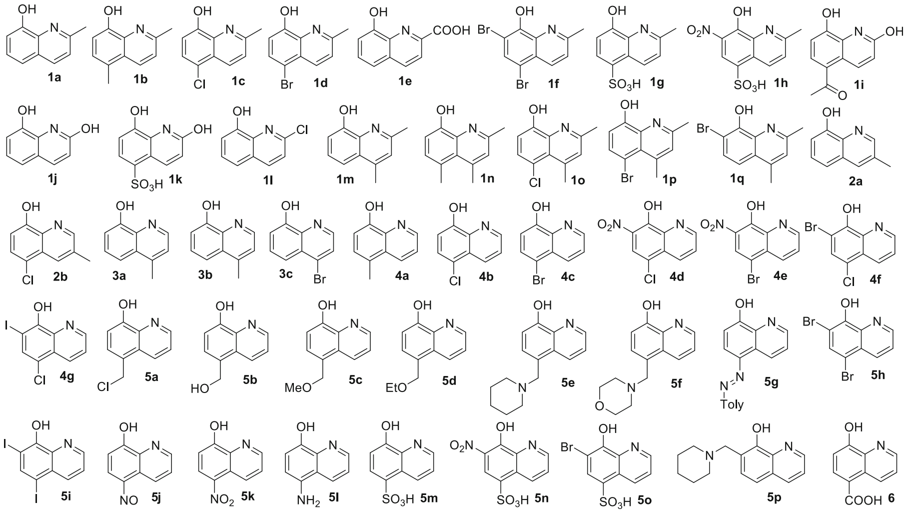
The fluorescence parameters of the 46 metal zinc compounds were measured, in which 8 compounds exhibited improved fluorescence intensity than 8-hydroxyquinoline and 28 compounds exerted decreased even no fluorescence intensity than 800. Among them, the emission wavelengths of 2 compounds were red-shifted and the wavelength of 17 compounds were blue-shifted. The influence of different substituents of 8-hydroxyquinoline on fluorescence emission wavelengths and intensity were discussed below.

The Substituents of 8-hydroxyquinoline Resulted in Red Shift of λem

The emission wavelengths of 2 compounds, which had been introduced halogen substituted groups on the benzene ring of 8-hydroxyquinoline, were all red-shifted (Fig. 2). The fluorescence data and corresponding fluorescence spectra of these compounds were as following:

When the C-5 of 8-hydroxyquinoline was replaced by chlorine or bromine, the fluorescence emission wavelengths of the corresponding zinc complexes were redshifted from

Fig. 1 The structures of ligands



553 nm to 569 nm and 568 nm respectively (Table 1, Entries 1~2).

It has been reported that the light emission of 8-hydroxyquinoline metal complex 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 Znq$_2$. Generally speaking, the highest electron density of Znq$_2$'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 [13–16].

The red shift was mainly caused by the introduction of a π-electron-rich substituent such as halogen at the C-5 position [17–19]. When the C-5 of 8-hydroxyquinoline was substituted by halogen groups, the HOMO value of the corresponding zinc complexes would be lower than the HOMO value of 8-hydroxyquinoline zinc complex and the energy gap between the HOMO and LUMO was reduced, so the fluorescence emission wavelengths of 8-hydroxyquinoline derivatives zinc complexes of **4b** and **4c** had been red-shifted.

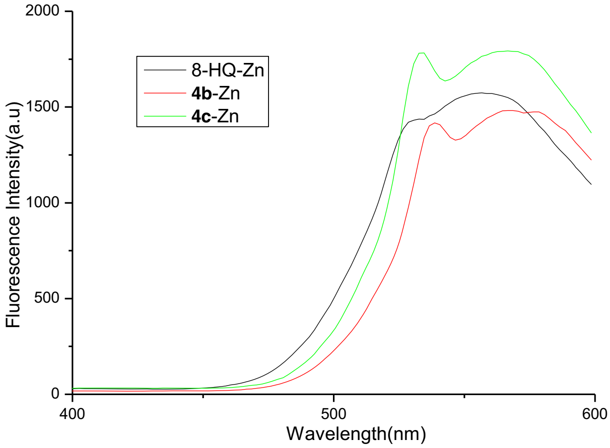


Fig. 2 Fluorescence spectra of 8-hydroxyquinoline derivatives zinc complexes with red-shifted emission wavelength in MeOH at 2×10^{-5} mol/L

The above data showed that some of the emission spectra have multiple peaks. This suggests multiple transitions. This result indicated that the ligands **4b** and **4c** can coordinate well with Zn(II) ions. The emission peaks at 505 nm and 600 nm were attributed to the $^5D_0 \rightarrow {}^7F_1$ (magneticdipole transition) and $^5D_0 \rightarrow {}^7F_2$ (electric dipole transition) of Zn(II) ions, respectively. It is known that the $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole transition) in the europium complex is almost independent of the ligands environment, whereas the $^5D_0 \rightarrow {}^7F_2$ (electric dipole transition) is sensitive to the coordination environment. The ligand in the Zn(II) complex absorbs energy and undergoes a π–π* transition, the electron transitions from the ground state of the singlet state to the lowest excited singlet state, then intersystem crossing occurs to the excited state of the triplet state in a non-radiative manner. The excited state of triplet state transfers energy to the vibrational energy level of the europium ion by the vibrational coupling of the chemical bond.

The Substituents of 8-hydroxyquinoline Resulted in Blue Shift of λem

In the fluorescence characterization, seventeen 8-hydroxyquinoline derivatives zinc complexes with blue-shifted fluorescence emission wavelengths were found (Fig. 3). The

Table 1 Fluorescence data of 8-hydroxyquinoline derivatives zinc complexes with red-shifted emission wavelength

Entry	Ligand	λex nm	λem nm	Intensity
1	8-HQ	264	553	1703
2	4b	265	569	1492
3	4c	265	568	1794

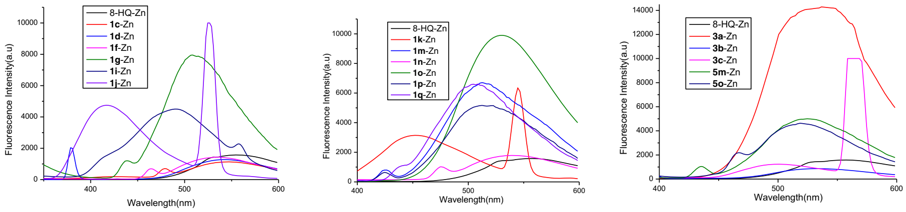


Fig. 3 Fluorescence spectra of 8-hydroxyquinoline derivatives zinc complexes with blue-shifted emission wavelength in MeOH at 2×10^{-5} mol /L $^{-5}$ mol/L

fluorescence data and corresponding fluorescence spectra of their zinc complexes are as following:

The maximum emission peaks shows that a good correlation exists between the electron withdrawing and donating nature of the substituent group on the 8-hydroxyquinoline and emission wavelength [17]. The electron-donating groups were introduced to pyridine ring or electron-withdrawing groups were introduced to benzene ring all would led to a fluorescence emission wavelength blue shift of zinc complexes [20, 21]. Due to existence of hydroxyl group at quinoline benzene ring, resulted in the molecule electron richer. The ligands with different electron-withdrawing groups, such as acetyl group and sulfonic acid group, were introduced to benzene ring, the electron cloud of benzene ring was deflected, the electron cloud of quinoline ring moved toward the substituents, the distribution of electron cloud in the whole molecular structure was uneven, which led to the increase of HOMO value of quinoline benzene ring. The energy gap between HOMO and LUMO increased, and the fluorescence emission wavelength of compounds had a blue shift, such as compounds **1i, 1 k**, **5 m** and **5o (**Table 2, Entries 2~4**)**. The addition of methyl and hydroxyl groups at C-2 position of the pyridine ring, such as ligands **1c**, **1d**, **1f**, **1 g**, **1i**, **1j**, and **1 k**, produced a certain spatial steric resistance to the molecular structure of the complex, which were not conducive to the binding of the ligand to the metal to form a stable five member ring structure. At the same time, the *N* atom of pyridine ring had a solitary pair of electrons, and this atom was directly involved in the complexation of the metal. If electron-donating groups were introduced to its *ortho* position, the distribution of electron cloud would transform, significantly alter the LUMO value, expanded the gap between HOMO and LUMO, which resulted in a significant blue shift of fluorescence emission wavelength. Therefore, when electron-donating groups were introduced into C-2 position on pyridine ring, the wavelength of complexes had a significant blue shift **(**Table 2, Entries 2~8**)**.

Table 2 Fluorescence data of 8-hydroxyquinoline derivative zinc complexes with blue-shifted emission wavelength

Entry	Ligand	λex nm	λem nm	Intensity
1	8-HQ	264	553	1703
2	1c	237	550	1148
3	1d	377	540	1277
4	1f	231	536	1444
5	1 g	216	515	7953
6	1i	227	491	4507
7	1j	260	416	4442
8	1 k	270	452	3118
9	1 m	210	512	6704
10	1n	235	545	1792
11	1o	374	531	9894
12	1p	210	513	5170
13	1q	216	510	6609
14	3a	259	537	14,289
15	3b	386	532	875
16	3c	280	500	1248
17	5 m	215	527	5000
18	5o	230	519	4632

A blue shift of fluorescence emission wavelengths of compounds **1 m**, **1n**, **1o**, **1p**, **1q**, and **3a**, for which the methyl at C-4 position [22]. Among them, **1 m** had more blue shift λem than **3a**, for them joint action of substituents at C-2 and C-4 position, not as **3a** only methyl at C-4 position (Table 3, Entries 9, 14**)**. Compared with compound **3a**, the blue shift of **1n** was weaker, which was due to the effect of methylsubstituent at C-5 position **(**Table 2, Entries 10, 14**)**.

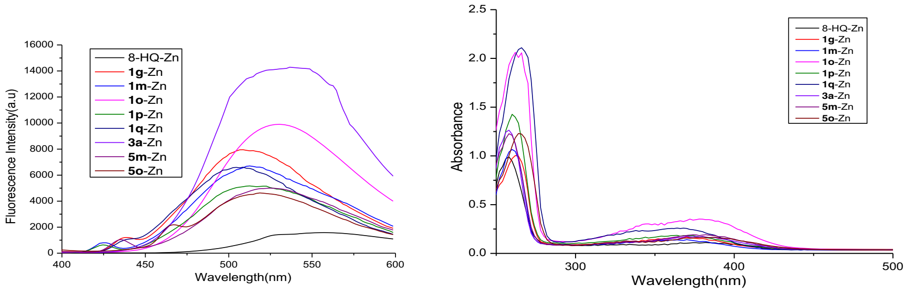
For ligand **5 m** was effected only by sulfonic acid group at C-5 position and **1 g** was effected by sulfonic acid group at C-5 position and hydroxyl group at C-2 position **(**Table 2, Entries 5, 17**)**, so **1 g** had more blue shift λem than **5 m** (Table 2, Entries 3,4).

The blue-shifted of the fluorescence wavelengths was due to the destabilizing action of the methyl group onto the pyridine ring on the LUMO value and the conjugation effect of the substituents onto the phenoxy ring on the HOMO [20–23], the energy gap between the HOMO and LUMO of the zinc complexes had an increase compared to that of 8-hydroxyquinoline zinc complex, so the fluorescence emission wavelengths of the above complexes had been blue-shifted.

The Fluorescence Intenstiy of 8-Hydroxyquinoline Derivatives Zinc Complexes

There were eight 8-hydroxyquinoline derivatives zinc complexes which owed high fluorescence intensity and they were also characterized by UV spectroscopy analysis using 8-hydroxyquinolone zinc complexes as contrast (Fig. 4). The

Fig. 4 Fluorescence spectra and UV of 8-hydroxyquinoline derivatives zinc complexes with high fluorescence intensity in MeOH at 2×10^{-5} mol/L



fluorescence data and corresponding fluorescence spectra and UV spectra of their zinc complexes are as following:

Furthermore, close inspection of the data in Table 3 reveals that the fluorescence quantum yield (ϕ) of complexes **3a**, **1o**, **1 g**, **1 m**, **1q**, **1p**, **5 m**, **5o** and **1n** depend on the electronic properties of the substituted methyl, halogen and sulfonic acid group moieties connected to C-4, C-5 and C-7 of 8-HQ. For instance, the fluorescence quantum yield of the eight complexes has increased significantly relative to the parent 8-HQ from 20% in the case of **1n** to 842% for **3a**.

When methyl was introduced into C-4 position on 8-hydroxyquinoline pyridine ring, the fluorescence intensity of compound was obviously enhanced. The fluorescence intensity of **3a** was almost 10 times better than 8-hydroxyquinoline (Table 3, Entry 1). The fluorescence quantum yields of **3a** was 0.377, which far greater than 0.040 of 8- hydroxyquinoline zinc (Table 3, Entry 1).

When the C-2 or C-4 of 8-hydroxyquinoline was substituted by methyl group or the C-5 was substituted by halogen and sulfonic acid group, the corresponding zinc complexes exhibited high fluorescence intensity and fluorescence quantum yields compared with 8-hydroxyquionline zinc complex (Table 3, Entries 2~8). We speculated that the introduction of a methyl group at C-4 position of 8-hydroxyquinoline or the introduction of a sulfonic acid group at the C-5 position would change the LUMO value and the HOMO value of the complexes [14, 23, 24]. Larger LUMO and HOMO value resulted in the confinement of holes and electrons in the organic light-emitting layer, which increased the electron-hole recombination efficiency. At the same time, the mobility of electrons in the framework of the complex was enhanced and the internal electronic transitions got reduced, so the corresponding zinc complexes owed high fluorescence properties.

Table 3 Fluorescence data of 8-hydroxyquinoline zinc complexes

Entry	Ligand	λex nm	λem nm	Intensity	ϕ
1	3a	259	537	14,289	0.377
2	1o	374	531	9894	0.248
3	1 g	216	515	7953	0.226
4	1 m	210	512	6704	0.174
5	1q	216	510	6609	0.153
6	1p	210	513	5170	0.138
7	5 m	215	527	5000	0.130
8	5o	230	519	4632	0.116
9	1n	235	545	1792	0.048
10	8-HQ	263	556	1574	0.040
11	1a	271	–	<800	<0.010
12	1 h	247	–	<800	<0.010
13	5n	265	–	<800	<0.010

"-" means the fluorescence intensity was too low to get the accurate value

The ligands **1 g**, **1 m**, **1o**, **1p**, **1q** and **1a**, which were all substituted by methyl at C-2 of 8-hydroxyquinoline, had different fluorescence properties. The ligands **1 g**, **1 m**, **1o**, **1p** and **1q** owed high fluorescence properties (Table 3, Entries 2~6), however the fluorescence property of **1a** was not good (Table 3, Entry 11), which confirmed that excellent fluorescent properties of **1 g** and **1 m** were caused by the introduction of sulfonic acid group at the C-5 of 8-hydroxyquinoline and the introduction of the methyl group at C-4 position. The excellent fluorescent properties of **1o**, **1p** and **1q** were caused by the introduction halogen at C-5 and C-7. When halogens are added via a heavy atom effect, which would be helpful to have available molecular structures of the HOMO and LUMO electron densities, which resulted good fluorescent properties.

When 8-hydroxyquinoline was substituted by introducing sulfonic acid group at C-5 position, such as **1 g**, **5 m** and **5o** (Table 3, Entries 3, 7, 8), their zinc complexes exhibited good fluorescence properties. But **1 h** and **5n** due to the introduction of a nitro group at C-7 position, the electron mobility of its zinc complex skeleton was weakened and the electron-hole recombination efficiency was reduced, so **1 h** and **5n** owed poorer fluorescence properties.

Conclusion

The 8-hydroxyquinoline ligands of zinc compounds with different substituents or different positions had different fluorescence properties. Firstly, when C-5 of 8-hydroxyquinoline was replaced by halogen, the fluorescence emission wavelengths of the corresponding zinc complexes had been red-shifted. Secondly, when the C-5 position of 8-hydroxyquinoline was substituted by electron-withdrawing groups, the fluorescence wavelengths of their zinc complexes had been blue-shifted.

Besides. Thirdly, when the C-4 position of 8-hydroxyquinolie was substituted by methyl or the C-5 position was substituted by sulfonic acid group, the corresponding zinc complexes owed high fluorescence intensity, which due to the mobility of electrons in the framework of the complex was enhanced and the internal electronic transitions got reduced.

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