**Research Paper** 



Theoretical and experimental studies on the fluorescence properties of aluminum(III), cadmium(II), zinc(II), and copper(II) complexes of substituted 8-hydroxyquinoline Journal of Chemical Research 1–12 © The Author(s) 2020 Article reuse guidelines: sagepub.com/journals-permissions DOI: 10.1177/1747519820973601 journals.sagepub.com/home/chl



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### Abstract

Fifty-five 8-hydroxyquinoline (8-HQ) derivatives are synthesized and the corresponding aluminum(III), cadmium(II), copper(II), and zinc(II) metal complexes are prepared and their fluorescent activities are evaluated. The results indicate that the aluminum complexes have the best fluorescence properties, followed by zinc and cadmium complexes, while almost no fluorescence is observed with the copper complexes. The relationship between the fluorescence properties and complex structure is summarized and a predictive three-dimensional quantitative structure–property relationship model is established using the multifit molecular alignment rule of Sybyl program. With the introduction of groups at the C-2 position or electron-withdrawing groups to the 8-hydroxyquinoline framework, fluorescence wavelength blue shifts are observed with the zinc, aluminum, and cadmium complexes. At the same time, a red shift of the fluorescence emission wavelength is detected for the aluminum and zinc complexes when C-5 of 8-hydroxyquinoline was substituted with halogens or a methyl group. Moreover, the zinc, cadmium, and aluminum complexes with 2,4-dimethyl substituents on the 8-hydroxyquinoline all show good fluorescence properties. The highest occupied molecular orbital and lowest unoccupied molecular orbital energies of the complexes are also calculated and the fluorescence properties of the metal complexes are analyzed from the viewpoint of molecular orbitals.

### **Keywords**

3D-QSPR, 8-hydroxyquinoline derivatives, aluminum complexes, cadmium complexes, copper complexes, fluorescence, zinc complexes

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### Introduction

Organic light-emitting diodes (OLEDs) are highly soughtafter by researchers in the monitor and lighting fields, and developing new luminescent materials with good properties has become an important area of research.<sup>1–5</sup> 8-Hydroxyquinoline, which possesses a heterocyclic conjugated planar structure, was used in multiple areas because of its chelating performance, luminescence properties, and

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Figure 1. The structures of the previously prepared 8-hydroxyquinoline derivatives.

coordination abilities.<sup>6</sup> Despite many efforts having been made on the preparation of 8-hydroxyquinoline derivatives and their metal complexes,<sup>7–12</sup> only a limited number of comparative studies are available on the influence of different substituents on the 8-hydroxyquinoline framework and different metals on the fluorescence properties of the corresponding complexes. Recently, we reported the synthesis of 55 different substituted 8-hydroxyquinolines (Figure 1) along with preliminary studies on the fluorescent properties of their zinc complexes.<sup>13</sup>

For a comparative study on the fluorescence properties of quinolines with different substituents and different central metals, a series of 8-hydroxyquinoline complexes with aluminum(III), cadmium(II), zinc(II), and copper(II) was prepared using the substituted 8-hydroxyquinolines shown above as ligands (Scheme 1).

The luminescence properties of the aluminum(III), cadmium(II), zinc(II), and copper(II) complexes were determined by fluorescence spectroscopy. The experimental results demonstrated that different substituents on the quinoline ring and different central metals had diverse influences on the fluorescence properties.

To our knowledge, there are no previous studies on the theoretical and experimental fluorescence properties of metal complexes of 8-hydroxyquinoline with different substituents. In the present work, a combined experimental and theoretical method was used to investigate the fluorescence spectral properties of 8-hydroxyquinoline derivatives, and provides a useful tool in designing metal complexes of 8-hydroxyquinoline by correlating theoretical optical properties with their experimental values.

## **Results and discussion**

In general, the fluorescence intensities of the 8-hydroxyquinoline aluminum complexes were the highest. Those of the zinc and cadmium complexes were very similar and weaker than those of the corresponding aluminum complexes. Fluorescence was barely observed for the copper complexes of the 8-hydroxyquinoline.

The fluorescence emissions of the 55 aluminum compounds were measured, 5 of which showed better fluorescence intensity than 8-hydroxyquinoline with fluorescence quantum yields ( $\phi_f$ ) above 0.171. Among the 22 complexes in which fluorescence was observed, the emission wavelengths of eight compounds were red-shifted and the wavelengths of 14 compounds were blue-shifted. Compared with aluminum complexes, nine zinc complexes exhibited



Scheme I. Preparation of substituted 8-hydroxyquinoline Al(III), Cu(II), Cd(II), and Zn(II) complexes.

Entry	Ligand	UV	Fluorescen	ce	Intensity				
		λmax (nm)	λex (nm)	λem (nm)	$2 \times 10^{-5}  mol  L^{-1}$	$2 \times 10^{-6}  \text{mol}  \text{L}^{-1}$	$2 \times 10^{-7} \text{mol } \text{L}^{-1}$		
1	lk	272	273	417	>10,000	>10,000	3700	0.990	
2	lp	246	256	468	>10,000	>10,000	400	0.969	
3	lq	258	262	464	>10,000	5200	-	0.572	
4	lr	252	260	492	>10,000	5000	-	0.540	
5	lo	248	260	502	>10,000	600	-	0.249	
6	8-HQ	252	370	510	>10,000	400	-	0.171	
7	3a	258	370	496	1780	-	-	0.0195	

Table 1. The fluorescence and UV data of the aluminum complexes with 1k, 1q, 1p, 1r, and 1o and 8-HQ under different concentrations.

improved fluorescence intensities in comparison to 8-hydroxyquinoline. Among the 16 zinc complexes in which fluorescence was observed, the emission wavelengths of three compounds were red-shifted and those of the remaining 13 compounds were blue-shifted. The fluorescence properties of the cadmium complexes were very similar to zinc, albeit the fluorescence intensity was weaker. There were eight cadmium complexes which exhibited improved fluorescence intensity compared to 8-hydroxyquinoline, and the emission wavelengths of them all were blue-shifted. Fluorescence was barely observed with the copper complexes, even with 8-hydroxyquinoline (8-HQ). The influence of different central metals and different substituents on the 8-hydroxyquinoline on the fluorescence emission wavelengths and intensities are discussed below.

### The effects of substituents on 8-hydroxyquinoline on the fluorescence intensity

The fluorescence data of the aluminum complexes with 1k, 1q, 1p, 1r, and 1o having the greatest fluorescence intensities are listed in Table 1 (see also Figure 2). In order to clearly distinguish the fluorescence intensity of these compounds, the concentration of solutions was diluted.

The fluorescence intensities of the aluminum complexes were 1k > 1p > 1q > 1r > 1o > 8-HQ (Table 1). The  $\varphi_{\scriptscriptstyle \rm f}$  values of the five complexes increased significantly compared with the parent compound 8-HQ, by 46% in the case of 10 to 475% for 1k. When a piperidyl moiety was introduced at C-2 of 8-HQ, the fluorescence intensity was obviously enhanced. Even when the solution of compound **1k** was diluted to  $2 \times 10^{-6} \text{ mol L}^{-1}$ , the fluorescence intensity was still more than 10,000 (Table 1, entry 1). After further diluting to  $2 \times 10^{-7} \text{ mol } \text{L}^{-1}$ , compound 1k still had a relatively strong fluorescence, while the other compounds had almost no fluorescence. The compounds with fluorescence intensities stronger than 8-hydroxyquinoline were methylated at C-2 and C-4 positions (Table 1, entries 2-6). Among them, ligands 1p and 1q having bromo groups at the C-5 and C-7 positions on quinoline benzene ring had better fluorescence intensities (Table 1, entries 2 and 3).

There were nine 8-HQ derivatives of zinc complexes possessing high fluorescence intensities and these were also characterized by UV spectroscopy analysis (Figure 3). The fluorescence spectra and UV spectra of their zinc complexes are shown below.

Furthermore, the data in Table 2 reveal that the  $\phi_f$  values of complexes 3a, 1o, 1e, 1n, 1q, 1p, 4q, 5d, and 1r were



**Figure 2.** Fluorescence (left) and UV (right) spectra of aluminum complexes with **1k**, **1q**, **1p**, **1r**, and **1o** and 8-HQ in  $2 \times 10^{-6}$  mol L<sup>-1</sup> MeOH.



**Figure 3.** Fluorescence (left) and UV (right) spectra of 8-hydroxyquinoline derivative zinc complexes with high fluorescence intensities in MeOH at  $2 \times 10^{-5}$  molL<sup>-1</sup>.

**Table 2.** The fluorescence and UV data of zinc complexes with **3a**, **Io**, **Ie**, **In**, **Iq**, **Ip**, **4q**, **5d**, **Ir**, and 8-HQ at a concentration of  $2 \times 10^{-5}$ mol L<sup>-1</sup>.

Entry	Ligand	UV	Fluore	scence	Intensity	$\varphi_{f}$	
		λmax (nm)	λex (nm)	λem (nm)	$\frac{1}{2 \times 10^{-5} \operatorname{mol} L^{-1}}$		
I	3a	256	259	537	14,289	0.377	
2	lo	262	374	531	9894	0.248	
3	le	260	216	515	7953	0.226	
4	In	262	210	512	6704	0.174	
5	١q	260	216	510	6609	0.153	
6	lp	266	210	513	5170	0.138	
7	4q	258	215	527	5000	0.130	
8	5d	258	230	519	4632	0.116	
9	lr	260	235	545	1792	0.048	
10	8-HQ	260	263	556	1703	0.040	
	lk	257	237	-	<400	_	

dependent on the electronic properties and steric factors of substituents, for example, methyl, halogen, and sulfonic acid groups at the C-4, C-5, and C-7 positions of 8-HQ. For instance, the  $\phi_f$  values of the eight complexes increased significantly relative to the parent 8-HQ from 20% in the case of **1r** to 842% for **3a**. The  $\phi_f$  values of **3a** was 0.377, which is greater than that of 8-hydroxyquinoline (0.040) with zinc (Table 2, entries 1 and 10).

There were eight fluorescent 8-hydroxyquinoline cadmium complexes that were characterized by UV spectroscopic analysis using the 8-hydroxyquinolone cadmium complex for comparison (Figure 4). The fluorescence and UV spectra of the cadmium complexes are as follows.

The fluorescence intensities of the cadmium complexes of 8-hydroxyquinoline derivatives and 8-HQ were much lower than those of the corresponding aluminum and zinc complexes (Table 3). The complexes of **3a**, **1o**, **1e**, **1n**, **1q**, **1p**, **4q**, and **5d** all showed higher fluorescence intensities than 8-HQ. This is in good agreement with the zinc



**Figure 4.** Fluorescence (left) and UV (right) spectra of 8-hydroxyquinoline derivative cadmium complexes with high fluorescence intensity in MeOH at  $2 \times 10^{-5}$  mol L<sup>-1</sup>.

Table 3. The fluorescence and UV data of cadmium complexes of 3a, 1o, 1e, 1q, 1n, 4q, 5d, 1p, and 8-HQ at the concentration of  $2 \times 10^{-5}$  mol L<sup>-1</sup>.

Entry	Ligand	UV	Fluore	scence	Intensity	$\varphi_{f}$	
		λmax (nm)	λex (nm)	λem (nm)	$2 \times 10^{-5}  \text{mol}  \text{L}^{-1}$		
I	3a	258	262	556	1785	0.048	
2	lo	262	374	544	1319	0.035	
3	le	262	218	526	1223	0.033	
4	١q	264	218	520	1099	0.029	
5	In	258	218	522	1031	0.028	
6	4q	256	218	530	1000	0.027	
7	5d	258	232	520	926	0.025	
8	lp	260	212	530	861	0.023	
9	8-HQ	260	263	_	<400	_	
10	lk	262	245	-	<400	-	

complexes, but the fluorescence intensities of the cadmium complexes were lower than those of zinc.

As almost all copper complexes of the 8-hydroxyquinoline derivatives were not fluorescence active, no further studies are discussed herein.

There are three compounds—10, 1p, and 1q—for which the zinc, cadmium, and aluminum complexes all showed good fluorescence properties (Table 1, entries 2, 3, and 5; Table 2, entries 2, 5, and 6; Table 3, entries 2, 4, and 8). Their common structural features were 2,4-dimethyl substitution of the parent 8-hydroxyquinoline. The introduction of substituents at C-2 and C-4 of the pyridine ring, such as in ligands 10, 1p, and 1q, produced a certain spatial steric resistance to the molecular structure of the complex, which was not conducive for metal binding and forming a stable five-membered ring structure. At the same time, the *N* atom of the pyridine ring, having lone pair electrons, was directly involved in complexation of the metal. Thus, steric hindrance has a great influence on the fluorescence properties.

Some zinc and cadmium complexes—such as those of 1k, 1e, 3a, 4q, and 5d—exhibited the corresponding

completely different fluorescence intensities compared with those of aluminum complexes. The aluminum complex of compound 1k exhibited good fluorescence intensity, while those zinc and cadmium showed lower fluorescence (Table 1 entry 1; Table 2 entry 1; Table 3 entry 10). The reason may be that the aluminum complexes were tri-coordinated and the piperidine could participate in metal complexation, while the 8-hydroxyquinoline zinc and cadmium complexes were bi-coordinated and piperidine ring was not involved due to the spatial relationships. In the aluminum complex of 1k, the piperidine ring had a strong electron-donating effect and formed a large  $p-\pi$  conjugation with quinoline ring, which made the conjugation effect over the whole molecule stronger and the fluorescence intensity increased. In addition, introduction of a piperidine ring increased the rigidity of whole molecular structure and reduced the molecular vibrations, which decreased the probability of collisions with other molecules and increased the fluorescence intensity.

However, with compound **3a** as the ligand, the zinc complex exhibited almost 10 times the fluorescence intensity of the 8-HQ zinc complex (Table 2, entry 1), and the fluorescence intensity of which was also the best for the cadmium complex (Table 3, entry 1). However, the fluorescence properties of the **3a** aluminum complex were not good, being almost 10 times worse than 8-HQ aluminum (Table 1, entry 7). When C-5 was substituted by a sulfonic acid group, such as in **1e**, **4q**, and **5d**, only the zinc and cadmium complexes exhibited high fluorescence intensities and fluorescence quantum yields (Table 2, entries 3, 7, and 8). The possible reason was that the rigidity of the zinc and cadmium complexes was greater than that of the aluminum complexes, and the introduction of a methyl group could stabilize the complexes.

## Three-dimensional quantitative structure– property relationship of the metal complexes

Three-dimensional quantitative structure-property relationship (3D-QSPR) analysis is widely applied due to its



Figure 5. 3D views of metal complex congeners by RMSD-based fitting.

Table 4. The statistical parameters for the 3D-QSPR CoMFA models<sup>a</sup>.

Entry	Complex	Statistical r	esults	Field contribution			
		R <sup>2</sup>	F	SE	q <sup>2</sup>	Steric (%)	Electrostatic (%)
1	Al	0.888	28.471	1.236	0.444	90.1	9.90
2	Zn	0.935	45.632	0.892	0.539	69.2	30.8
3	Cd	0.912	44.781	0.955	0.505	84.4	15.6

 $R^2$ : the predictive correlation coefficient; F: test value; SE: standard error of estimate;  $q^2$ : the leave-one-out (LOO) cross-validation coefficient. <sup>a</sup>Method is CoMFA.

well-established predictive power.<sup>14–16</sup> In particular, the comparative molecular field analysis (CoMFA) is an effective method based on statistical techniques.<sup>17</sup>

In order to further modify the molecule, 3D-QSPR studies were applied on the  $\phi_f$  using the CoMFA protocol for the first time. The data-based fitting procedure was finally adopted through careful comparison. Each metal complex, in which fluorescence could be observed, was superimposed to the template based on the common substructure of aluminum(III), cadmium(II), zinc(II), and copper(II) complexes of 8-hydroxyquinoline. The aligned molecules are illustrated in Figure 5, and the statistical parameters are listed in Table 4.

For metal complexes, as shown in Table 4, better predictions are obtained with 3D-QSPR/CoMFA for the absorption properties. The model has a high  $R^2$  value (0.935) for zinc complexes, with a low standard deviation (*SE*, 0.892) and a high Fischer's ratio (*F*, 45.632), while a QSPR model is generally acceptable if  $R^2$  is approximately 0.85 or higher. Specially, the cross-validation-related coefficient  $q^2$ is 0.4501 (>0.45), suggesting a good prediction ability of this model.

The contribution of the steric field of aluminum(III), zinc(II), and cadmium(II) is 90.1% (Table 4, entry 1), 69.2% (Table 4, entry 2), and 84.4% (Table 4, entry 3) and the electrostatic field of aluminum(III), zinc(II), and cadmium(II) is 9.90% (Table 4, entry 1), 30.8% (Table 4, entry 2), and 15.6% (Table 4, entry 3), respectively. This



Figure 6. Plots of experimental data versus the corresponding predicted data from the QSPR/CoMFA models.

showed that the steric hindrance has a significant influence on the fluorescence properties, especially the fluorescence properties of aluminum complexes which are almost determined by the steric factors. The plots of the predicted versus actual  $\phi_f$  value for the QSPR/CoMFA model are displayed in Figure 6, which shows a good correlation. The electrostatic field is the main factor influencing the maximum absorption.



**Figure 7.** Stereo views of CoMFA steric field and electrostatic field of metal complexes.

To view the field effect on the target property, CoMFA contour maps were generated and shown in Figure 7. For steric fields, green means that a bulky group is favorable and yellow indicates that a bulky group is unfavorable. Similarly, blue means that an electropositive charge is favorable and red indicates that an electronegative charge is favorable.

For example, for the aluminum complexes, the steric field of the complexes has green contours (75.80%) indicating sterically favored regions for fluorescence properties, and the yellow contours (24.20%) highlight the sterically unfavorable regions. The electrostatic field has blue contours (13.23%) representing electropositively preferred regions to better fluorescence performance, and red contours (86.77%) indicate regions where more electronegative substituents are favored to increase fluorescence. The data for the CoMFA steric field and electrostatic field of the cadmium and zinc complexes of 8-hydroxyquinoline are also shown in Figure 7.

# The substituents on 8-hydroxyquinoline resulted in a blue shift of $\lambda$ emission examples ( $\lambda$ em)

The  $\lambda$ em of the 13 aluminum and zinc complexes were both blue-shifted (Table 5). Seven of them were fluorescence

active as their cadmium complexes, which were blueshifted as well.

The blue shift of complex **1i** is 97 nm, which is the largest of the aluminum complexes, while that of the zinc complex is 137 nm which is also the largest among the zinc complexes (Table 5, entry 13). The largest blue shift in the cadmium complexes is compound **1q** with a blue shift of 70 nm (Table 5, entry 12). The blue shifts for different substituted compounds with different metal complexes were almost the same. The effect of substituents on the fluorescence wavelengths is discussed later. In terms of the blue shift of the maximum fluorescence emission wavelength, the results for the zinc, cadmium, and aluminum complexes were almost identical and the common points are discussed below.

The maximum emission indicated that the electron-donating and electron-withdrawing nature of the substituents on the 8-HQ and the emission wavelengths had a good correlation.<sup>18</sup> There were two factors causing the blue shifts of the aluminum, cadmium, and zinc complexes, which were the introduction of electron-donating groups on the pyridine ring and electron-withdrawing groups on the benzene ring.<sup>19,20</sup> The addition of substituents at C-2 of the pyridine ring, such as in ligands 1b, 1c, 1g, 1i, 1l, 1n, 1o, 1p, 1q, and 1r, produced a certain spatial steric resistance to the complex structure, which was not conducive to the formation of a stable five-membered ring structure. At the same time, the N atom of the pyridine ring, having a lone pair of electrons, was directly involved in complexation of the metal. A blue shift of the fluorescence emission wavelengths of compounds 1n, 10, 1p, 1q, 1r, and 3a with a methyl group at the C-4 position was observed.<sup>21</sup> Among them, **1n**, **1p**, **1q**, and **1r** had larger blue shifts  $\lambda$ em value than **3a**, which might be because they all had two substituents at C-2 and C-4 (Table 5, entries 8–12), while **3a** only has a methyl group at C-4 (Table 5, entry 7). Compared with compound 3a, the blue shift of 10 was weaker, which might be due to the effect of the chlorine substituent at C-5 (Table 5, entries 3 and 7).

In the same way, the  $\lambda$ em values of the zinc and cadmium complexes of **1e** were blue-shifted, but the wavelength of aluminum complexes could not be observed due to weak fluorescence (Table 5, entry 14). The structures of the above compounds were consistent with the previous blue shifts ligand, of which the electron-donating groups were introduced on the pyridine ring while the electronwithdrawing groups were introduced on the benzene ring.

## The substituents on 8-hydroxyquinoline resulted in a red shift of $\lambda$ emission examples ( $\lambda$ em)

Since no red shift was observed in the cadmium complexes, only zinc and aluminum complexes were compared and discussed. The emission wavelength of nine aluminum complexes was red-shifted, while three of the nine zinc complexes were red-shifted. The wavelengths of the aluminum and zinc complexes of **2d**, **4m**, and **4n** were red-shifted. The fluorescence data for these compounds are given in Table 6.

When halogens or methyl groups were introduced at the C-5 position of 8-hydroxyquinoline, the fluorescence

Entry	Ligand	and Aluminum complexes			Zinc comp	Zinc complexes			Cadmium complexes		
		λex (nm)	λem (nm)	Intensity	λex (nm)	λem (nm)	Intensity	λex (nm)	λem (nm)	Intensity	
I	8-HQ	370	510	>10,000	264	553	1703	263	590	<400	
2	lg	268	507	1400	231	536	1444	_	_	<400	
3	lo	260	502	>10,000	374	531	9894	374	544	1319	
4	lb	263	501	2730	237	550	1148	_	_	<400	
5	lc	263	499	1600	377	540	1277	_	_	<400	
6	4q	210	497	1490	215	527	5000	218	530	1000	
7	3a	370	496	1780	259	537	14,289	262	556	1785	
8	lr	260	492	>10,000	235	545	1702	_	_	<400	
9	In	260	490	600	210	512	6704	218	522	1031	
10	П	260	471	1640	270	452	1688	_	_	<400	
11	lp	256	468	>10,000	210	513	5170	212	530	861	
12	Ig	262	464	>10,000	216	510	6609	218	520	1099	
13	li	259	413	1690	260	416	1442	_	_	<400	
14	le	270	-	<400	216	515	7953	218	526	1223	

**Table 5.** Data for the aluminum, cadmium, and zinc complexes both with blue shifted of  $\lambda$ em.

**Table 6.** Data for the aluminum and zinc complexes both red-shifted  $\lambda em$ .

Entry	Ligand	Aluminum co	mplexes		Zinc complexes		
		λex (nm)	λem (nm)	Intensity	λex (nm)	λem (nm)	Intensity
1	2d	233	539	2078	210	570	2100
2	4m	384	528	1990	265	569	1492
3	4n	234	522	1870	265	568	1694
4	41	232	538	1300	256	_	<400
5	4a	370	532	1490	261	_	<400
6	5g	242	522	2150	261	_	<400
7	5f	225	517	1279	235	_	<400
8	2b	383	531	1300	260	_	<400
9	8-HQ	370	510	>10,000	264	553	1703

8-HQ: 8-hydroxyquinoline.

emission wavelength of the corresponding metal aluminum and zinc complexes was red-shifted. Compared with the  $\lambda$ em of the 8-HQ aluminum complex (Table 6, entry 9), the fluorescence emission wavelengths of compounds 2d, 4m, and 4n with methyl, chlorine, and bromine substituents, respectively, at the C-5 position of quinoline, exhibited changes in the range of 12–29 nm for the red shifts of the aluminum complexes, and 15–17 nm red shifts for the zinc complexes (Table 6, entries 1–3).

The fluorescence wavelengths of the aluminum complexes of **2b**, **4a**, **4l**, **5g**, and **5f** were red-shifted too (Table 6, entries 4–8). The common feature was a methyl or halogen group at C-5 of the 8-hydroxyquinoline. For the zinc complexes of **2b**, **4l**, **4a**, **5g**, and **5f**, the fluorescence intensities were less than 400 and thus almost fluorescent inactive.

## Analysis of the effect of the structure on the fluorescence properties in terms of molecular orbitals

There are three compounds—10, 1p, and 1q—for which the zinc, cadmium, and aluminum complexes all showed good fluorescence properties. In Table 7, with 8-HQ as the

**Table 7.** Energies of the molecular orbitals and the  $\phi_f$  values of **10**, **1q**, and **1p**.

Entry	Metal	Ligand	$\varphi_{\rm f}$	E <sub>HOMO</sub> *	E <sub>LUMO</sub>	$E_{gap}$
1	AI	8-HQ	0.171	-0.18683	0.00791	0.19474
2		lo	0.249	-0.20389	0.00588	0.20977
3		١q	0.572	-0.20338	0.01523	0.21861
4		lp	0.969	-0.21896	0.01046	0.22942
5	Zn	8-HQ	0.040	-0.24034	0.01259	0.25293
6		lp	0.138	-0.24719	0.03914	0.28633
7		lq	0.153	-0.24363	0.04285	0.28648
8		lo	0.248	-0.28329	0.06099	0.34428
9	Cd	8-HQ	_	-0.23957	0.03951	0.27908
10		lp	0.023	-0.23972	0.04333	0.28305
П		lq	0.029	-0.24506	0.04115	0.28621
12		lo	0.035	-0.24636	0.04055	0.28691

\*The Hartree was used as the energy unit; energies in subsequent tables are also in Hartrees.

parent compound, the calculated values of the  $E_{HOMO}$ ,  $E_{LUMO}$ , and  $E_{gap}$  of the complexes of **10**, **1p**, and **1q** are given (Figure 8).



Figure 8. The HOMOs and LUMOs of metal complexes 8-HQ, Io, Ip, and Iq.

The effects of the different energies of the molecular orbitals on the fluorescence properties of the corresponding aluminum(III), cadmium(II), copper(II), and zinc(II) metal complexes are summarized as follows: the electron density of the pyridine ring was improved by the introduction of methyl groups at C-2 and C-4 of 8-HQ and would thus change the LUMO and HOMO values of the complexes.<sup>19,21</sup> At the same time, the N atom of the pyridine ring, having a lone pair of electrons, was directly involved in complexation of the metal. If electron-donating groups were introduced at ortho positions, the distribution of the electron cloud would be changed, which might significantly alter the LUMO value and expand the gap between the HOMO and LUMO. For example, the  $\phi_{\rm f}$ values of aluminum complexes from 8-HQ, 10, and 1p to 1q increased from 0.171, 0.249, and 0.572 to 0.969 and the E increased from 0.19474, 0.20977, and 0.21861 to 0.22942 (Table 7, entries 1–4), that is, the higher the  $E_{gap}$  value, the higher the  $\phi_f$  value. The same results were obtained for cadmium (Table 7, entries 9-12) and zinc metal complexes (Table 7, entries 5-8). A larger energy gap between the LUMO and HOMO resulted in the confinement of holes and electrons in the organic light-emitting layer, which could increase the electron-hole recombination efficiency. Finally, the molecular total energy was decreased, which facilitated the  $\pi$ - $\pi$ \* transition, increased the number of effective migrations, and enhanced the fluorescence intensity of the complexes. At the same time, the mobility of electrons in the framework of the complex was enhanced and the internal electronic transitions were reduced, so the corresponding metal complexes had high fluorescence properties.<sup>22</sup>

Another phenomenon was that the  $\lambda$ em values of the zinc, cadmium, and aluminum complexes, in which the fluorescence intensity was increased, almost showed blue shifts. This might due to the larger energy gap between the LUMO and HOMO of the above metal complexes.

The addition of substituents at the C-2 position of the pyridine ring, such as in ligands **1b**, **1c**, **1g**, **1i**, **1l**, **1n**, **1o**, **1p**, **1q**, and **1r** (Table 5, entries 3–11), results in a certain spatial steric resistance to the complex structure, which was not conducive to the formation of a stable five-membered ring structure. If electron-donating groups were introduced at *ortho* positions, the distribution of the electron cloud would change, which might significantly alter the LUMO value and expand the HOMO and LUMO gaps, such as in the zinc, cadmium, and aluminum complexes **1o**, **1p**, and **1q** (Table 7), which resulted in a significant blue shift of the fluorescence emission wavelength. Therefore, when electron-donating groups were introduced at C-2 position on the pyridine ring, the wavelength of the complexes had a significant blue shift.

However, the regularity of the wavelength changing with the  $E_{gap}$  is not as good as that of  $\phi_{f}$ . In order to analyze the cause of the blue shift of the metal complexes from the viewpoint of molecular orbitals, the HOMOs and LUMOs of complexes with similar structures were calculated and compared, and the results are shown in Figure 9 and Table 8.

The ligands, which possess different electron-withdrawing groups, such as sulfonic acid, could induce deflection of the electron cloud, which leads to an increase of the HOMO value of the quinoline benzene ring. As a result, the

HOMO LUMO HOMO LUMO Al Complexes Zn Complexes

Figure 9. The HOMOs and LUMOs of metal complexes 4q and 11.

Table 8. Energies of molecular orbitals and the  $\lambda em$  values of 4q and 11.

Entry	Metal	Ligand	λem	Е <sub>номо</sub>	E <sub>LUMO</sub>	$E_{gap}$
I	AI	8-HQ	510	-0.18683	0.00791	0.19474
2		4q	497	-0.23567	-0.03417	0.20253
3		П	471	-0.25381	-0.02341	0.23040
4	Zn	8-HQ	553	-0.24034	0.01259	0.25293
5		4q	527	-0.29282	-0.02636	0.26646
6		П	452	-0.29806	-0.02180	0.27626

8-HQ: 8-hydroxyquinoline.

energy gap between the HOMO and LUMO is increased, and the fluorescence emission wavelength of compounds had a blue shift, such as in compounds **4q** and **11** (Table 8). The  $E_{gap}$  of the aluminum and zinc complexes of **11** were 0.23040 and 0.27626, respectively, which are larger than those of the corresponding complex **4q**, so the fluorescence emission wavelength of **11** has a bigger blue shift than that of **4q** (Table 8, entries 2, 3, 5, and 6). Ligand **4q** was affected only by a sulfonic acid group at C-5 and **11** was affected by a sulfonic acid group at C-5 and by a hydroxy group at C-2 at the same time, so **11** had a greater blue shift of  $\lambda$ em than **4q**. The results are consistent with the  $E_{gap}$ analysis.

The luminescence of the 8-hydroxyquinoline metal complex was caused by the electron  $\pi$ - $\pi$ \* transition from the HOMO of the phenol ring to the LUMO located on the pyridyl ring.<sup>23</sup> The highest electron density of the HOMO of the 8-hydroxyquinoline metal complex was at the phenol oxygen and the C-5, C-7, and C-8 positions. Thus, it can be predicted that electron-withdrawing groups or electron-donating groups at these positions would lead to blue or red shifts of the absorption and fluorescence spectra.<sup>24</sup> There are three compounds, **2d**, **4m**, and **4n**, for which the fluorescence wavelength of the zinc and aluminum complexes was red-shifted. In Table 9, with 8-HQ as the parent compound, the E<sub>HOMO</sub>, E<sub>LUMO</sub>, and E<sub>gap</sub> of the complexes of **4m**, **4n**, and **2d** were calculated (Figure 10).

The  $E_{gap}$  of most of the red-shifted complexes was also larger than that of 8-hydroxyquinoline, and was irregular with the wavelength changes. However, we found that the

**Table 9.** Energies of the molecular orbitals and the  $\lambda$ em values of **2d**, **4m**, and **4n**.

Entry	Metal	Ligand	λem	Е <sub>номо</sub>	E <sub>LUMO</sub>	$E_{gap}$
1	AI	8-HO	510	-0.18683	0.00791	0.19474
2		4n	522	-0.22910	-0.00459	0.22451
3		4m	528	-0.23883	-0.00864	0.23019
4		2d	539	-0.24375	-0.00996	0.23375
5	Zn	8-HQ	553	-0.24034	0.01259	0.25293
6		4n	568	-0.25414	-0.00592	0.24822
7		4m	569	-0.26035	-0.00741	0.25294
8		2d	570	-0.26603	-0.01094	0.25509

8-HQ: 8-hydroxyquinoline.



Figure 10. The HOMO and LUMOs of metal complexes 2d, 4m, and 4n.

lower the HOMO value of the complexes, the greater the red-shifted fluorescence emission wavelength. For example, the HOMO of the aluminum complexes decreases from **4n**, **4m** to **2d** at -0.22910, -0.23883, and -0.24375, respectively, and the wavelength changes from 522, 528 to 539 (Table 9, entries 2–4). The HOMO of zinc complexes decreases from **4n**, **4m** to **2d** at -0.25414, -0.26035, and -0.26603, respectively, and the wavelength changes from 568, 569 to 570 (Table 9, entries 5–8).

When the C-5 position of the 8-hydroxyquinoline benzene ring was substituted with a halogen, such as in **4m** and **4n**, which has three lone pairs of electrons, it was easy to form a large  $p-\pi$  conjugation with the quinoline benzene ring, which led to a more uniform distribution of the electron cloud and decreased the HOMO value of substituted 8-hydroxyquinoline metal complex. The lower HOMO value led to the fluorescence emission wavelengths of the metal complexes being red-shifted. When a methyl group was introduced at C-5 of the 8-hydroxyquinoline, due to the electron donor effect, the HOMO value of the phenol ring decreased. The fluorescence emission wavelength of the metal complexes had a red shift.

11

## Conclusion

Fifty-five 8-hydroxyquinoline (8-HQ) derivatives were synthesized and the corresponding aluminum(III), cadmium(II), copper(II), and zinc(II) metal complexes were prepared and their fluorescent activities were evaluated. The aluminum complexes had the best fluorescence properties, followed by zinc. The fluorescence can also be observed in cadmium complexes, while almost no fluorescence was observed in copper complexes. The fluorescence properties of the few aluminum, zinc, and cadmium complexes were different. The 3D-QSPR model was proposed using CoMFA based on the molecular simulation, which also exhibited good stability and good prediction ability. The optimum models were statistically significant with cross-validated coefficients ( $q^2=0.444$ , 0.539, and 0.505) and conventional coefficients ( $R^2=0.888$ , 0.935, and 0.912), indicating that they were reliable enough for the prediction of the fluorescence quantum yields.

The relationship between the fluorescence properties and the complex structure has been summarized. The effects of the structure and energies of the molecular orbitals on the fluorescence properties were analyzed. The effect of the ligand substituents on the fluorescence properties of 8-hydroxyquinoline zinc, cadmium, and aluminum complexes shows some common points: first, the introduction of a halogen or a methyl group at C-5 of the 8-hydroxyquinoline ring results in a red shift of the fluorescence emission wavelength of aluminum complexes due to the increased conjugation effect and the decreased  $\mathrm{E}_{\mathrm{HOMO}}$ value. Second, when electron-withdrawing groups were introduced on the 8-hydroxyquinoline ring, the conjugation effect of the quinoline ring was decreased and the  $E_{gap}$  value increased, which led to a blue shift of the fluorescence emission wavelength and a weak fluorescence intensity. Third, a stronger intensity of the fluorescence would be achieved by introducing a methyl groups at position of 2 and 4 of the 8-hydroxyquinoline ring, which led to steric issues and a bigger gap between the HOMO and LUMO.

### Experimental

Details of the synthesis and characterization of ligands are provided in the supporting material. The procedures for the preparation of the zinc complexes and recording the fluorescence measurements are consistent with those of previous our report.<sup>13</sup>

General procedure for the preparation of the aluminum complexes. The 8-hydroxyquinoline ligand (1.0 mmol) was added to anhydrous methanol at room temperature, and then the temperature was raised to 70 °C. An aqueous solution of aluminum sulfate (1.0 mmol) was slowly added dropwise, and the mixture was maintained at 70 °C for 20 h. The pH of the mixture was adjusted with ammonia solution to about 7–8. After stirring for 4 h, the obtained precipitate was filtered and recrystallized from anhydrous methanol to give the pure product.

General procedure for the preparation of the cadmium complexes. A mixture of  $CdNO_3$  (0.5 mol), 8-hydroxyquinoline ligand (1.0 mmol), water, and MeOH in a capped vial was heated at 80 °C for 1 day. Colored block–like crystals were collected by filtration, washed with ether, and dried to give the desired product.

General procedure for the preparation of the copper complexes. A pale green solution of  $CuCl_2 \cdot 2H_2O$  (0.5 mmol) dissolved in methanol was added slowly to a solution of the 8-hydroxyquinoline ligand (1.0 mmol) in methanol. After stirring for 30 min, the solid was filtered, washed with ether, and dried to give the desired product.

Photoluminescence quantum yields. Quantum yields of fluorescence ( $\phi_f$ ) can be measured in two different ways: relative to a fluorescent standard material with a known  $\phi_f$  or as an absolute quantity. The measurement of relative fluorescence quantum yields has exclusively been done by optical methods, most prominently using a spectrofluorometer and the comparative method as proposed by Parker and Rees.<sup>25</sup> In this paper, the  $\phi_f$  was calculated by a comparative method using the following equation<sup>6,26,27</sup>

$$\Phi_{\rm f} = \frac{n_{\rm x}^2}{n_{\rm std}^2} \cdot \frac{F_{\rm x}}{F_{\rm std}} \cdot \frac{A_{\rm std}}{A_{\rm x}} \cdot \Phi f_{\rm std}$$

In this experiment,  $n_x$  was approximately equal to the refractive index of the solvent, the solvent used in this experiment was MeOH, so the  $n_x$  value was approximately 1.360, the  $n_{std}$  for the refractive of water index of water had a value of about 1.337. *F* denotes the integrated area in the fluorescence spectrum, and *A* denotes the absorbance in the ultraviolet spectrum.  $\phi f_{std}$  is the fluorescence quantum yield of the standard solution, quinine sulfate  $(1.0 \,\mu g \,m L^{-1})$  in sulfuric acid solution  $(0.1 \,mol \,L^{-1})$  was used as a standard reference, and the  $\phi f_{std}$  was 0.55. Fluorescence spectra were measured in MeOH solution, and the slit width was 5.0 nm.

*Computational details.* All computations of optimized geometry were carried out using the Gaussian  $09^{28}$  computer software package. The electronic descriptors were obtained from a single-point calculation at the B3LYP/6-311+g (d) level. The structural parameters—including the energy of highest occupied molecular orbital ( $E_{HOMO}$ ), the energy of the lowest unoccupied molecular orbital ( $E_{LUMO}$ ), and the energy difference between the LUMO and HOMO ( $E_{gap}$ )—were also calculated. 3D-QSPR studies on the metal complexes were performed using the literature procedure reported by us using CoMFA performed on the Sybyl 8.0 package.<sup>29</sup>

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### Supplemental material

Supplemental material for this article is available online.

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