SPECTROSCOPY LETTERS, 29(6), 995-1001 (1996)

EFFECT OF METAL CATION ON ABSORPTION AND FLUORESCENCE SPECTRA OF METAL COMPLEXES OF 8-HYDROXYQUINOLINE*

Key words : 8-hydroxyquinoline chelate of metal, absorption spectrum, fluorescence

L.G.Zhang, X.G.Ren, D.P.Jiang, A.D.Lu and J.S.Yuan

Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, China

Abstract

8-Hydroxyquinoline complexes of Na(I), Ca(II), Mg(II), Zn(II), Mn(II), Cu(II), Al(III), In(III) and La(III) are synthesized. Photoluminescence and UV-vis absorption spectra of them are reported. Except complexes of Cu(II), and Mn(II), these complexes show photoluminescence. With the increase of polarization force of metal cation, their photoluminescence peaks reveal red-shift and two broad absorption bands in UV-vis absorption spectra appear split and red-shift.

Introduction

In recent years, metal chelates of 8-hydroxyquinoline (MQ) played an important role in organic electroluminescence (OEL), especially, tri(8-hydroquinolinolato) aluminum (AlQ) was widely introduced in OEL cell as

*The work was supported by Chinese Academy of Sciences.

emission layer[1,2,3], and the others such as ZnQ and BeQ also were used in OEL cell[2]. The metal chelates of 8-hydroquinoline arouse wide interesting because of their novel structure and fluorescence characteristics[4,5].

The present paper reports a study of the absorption spectrum and photoluminescence (PL) characteristics of MQ. This is intended to provide the useful information for spectra change of MQ with different cations.

Experimental

We synthesized 8-Hydroquinoline chelates of Na(I), Ca(II), Mg(II), Zn(II), Cu(II), Mn(II), Al(III), In(III) and La(III) (below referred to as NaQ, CaQ, MgQ ···, respectively) by traditional process. HQ complexes of Zn, Mg, Ca, La, In and Al were purified by the means of washing in methyl alcohol.

UV--vis absorption spectra of HQ and metal chelates of HQ in trichloromethane were measured on UV-360 spectrophotometer. Emission spectra of these metal chelates powder were recorded on MPF--4 fluorescence spectrophotometer.

Results

Of all metal chelates in experiment, HQ complexes of Ca, Na, Zn, Mg, In, Al and La show photoluminescence (PL). These PL spectra generally present board-band with a single peak and full width at half maximum of 80nm--100nm. The PL peaks of these complexes list in table 1, ranging from 470nm to 530nm. Whereas, PL intensity of CuQ and MnQ were too weak to observe. Fig. 1 shows the PL of CaQ excited under 365nm.

Absorption spectra of HQ and MQ have a narrow strong absorption band at about 240nm respectively, which is composed of two peaks located rather closely, and two broad absorption bands overlapping together between 300nm and 400nm. The effect of different cation chelated on the narrow-band absorption is far less than that on the two broad absorption bands, as shown in Fig.2

Comparing the PL peak with broad absorption band in 300nm - 400nm listed in table 1, we find out there is a relationship between them. Red-shift of PL from MQ are in accordance with separation and red-shift of the two

Table 1. The peaks of PL and absorption spectra for MQ

MQ	CaQ	NaQ	LaQ	ZnQ	MgQ	AlQ	InQ	CuQ	HQ
PL peak (nm)	475	485	506	516	518	522	530		
Absorption peak in 300-400nm (nm)	310 350	310	304 320	320 375	330 380	310 380	320 380	400	304

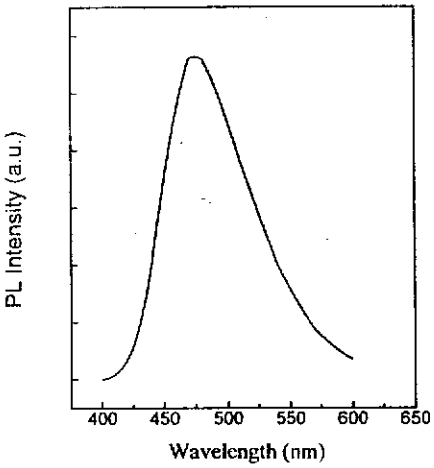

Figure 1. PL spectrum of CaQ powder excited under 365nm.

broad absorption bands for the corresponding chelate. InQ and AlQ have two obviously separate broad absorption bands between 300nm and 400nm. Whereas, CaQ and NaQ are observed a large overlapping broad absorption bands in the above range.

HQ's absorption spectrum within 300- 400nm reduces into a single broad band with a peak at 300nm.

Discussion

UV-vis absorption spectra of 8-hydroxyquioline complexes of metal obviously reveal 3 bands of absorption. One located near 240nm is a narrow

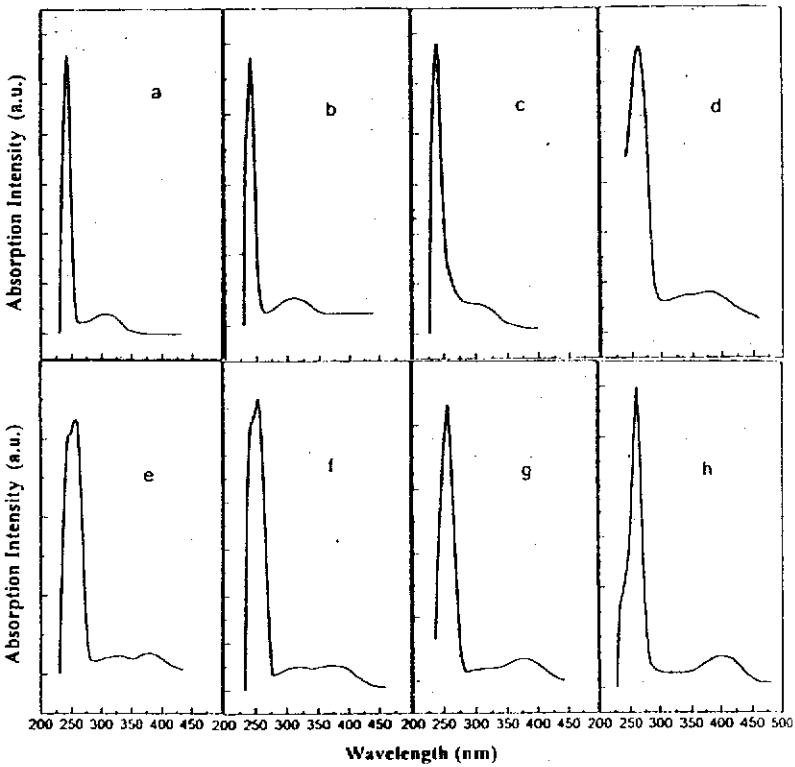

Figure 2. UV-Vis absorption spectra of HQ and MQ. These spectra respectively present the following materials: a: HQ, b:NaQ, c: CaQ, d: ZnQ, e: MgQ, f: InQ, g: AlQ, h: CuQ.

strong absorption band, which indicates molecular transition of $\sigma \rightarrow \sigma^*$. And the other two broad absorption bands in the range of 300nm – 400nm overlapping together indicate $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively. Owing to 8-hydroxyquinline ring as a large conjugate system, for HQ, its energy band is widen so that energy of molecular orbit of n and π is approximate and molecular orbit superimpose, leading to a single absorption band within 300nm--400nm. In MQ, the interaction of the empty-orbit in metal cations with the solitary pair electrons (N electron) in Nitrogen atom varies energy of

excited and base state of N electron orbit. Moreover the excited state energy of π electron lowers by π and N electron coupling, thus resulting in absorption spectra relative to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ red shift.

Hydrogen in HQ can't couple N electron in nitrogen atom to form hydrogen-bond and HQ molecule can't chelate into a planar structure, because it is difficult for hydrogen atom in hydroxyl group to form bare proton due to conjugating effect of HQ ring. Thus, internal freedom degree of HQ molecule is larger than that of MQ. Molecule with large internal freedom degree easily deform so that the probability of HQ molecule transition from excited state to base state via multiphone process enlarges and the efficiency of fluorescence decreases.

Meanwhile, all atoms in MQ locate in one plane because metal cation chelate with Nitrogen atom. Planar structure is suitable for intersection of electrons cloud and reduces the internal freedom degree of molecule, so such structure can decrease entropy of molecules. The probability of nonradiative transition is lowered because the planar structure make it difficult for molecule to deform. In this experiment, most of MQ reveal PI, but HQ doesn't.

The effect of metal cation on solitary pair electrons and π electrons depends on the polarization force of metal cation. Experimentally, the polarization force of metal cation is deeply relative to the cation radius, the ion valence and bond's covalence. The cation with large ratio of ion charge to radius and low covalence of bond possesses strong polarization force. The ratioes of Cation charge to radius are listed in table 2[6]. Taking account of the above factors of cation, we conclude that aluminum and indium ions have stronger polarization force, but sodium and calcium cation possess weaker polarization force.

Cation can intensely interact with the solitary pair electrons in nitrogen and the π electron cloud in quinoline ring when it has strong polarization force, so that energy of the excited state of molecule obviously decrease. This corresponds to the fact that the emission and absorption spectra of MQ show red shift with the strength of polarization force of cation.

PI. of CuQ and MnQ aren't observed, and LaQ has very low florescence efficiency. These probably concerned in d, f electron.

Table 2. the ratioes of ion charge to radius related to the cations in experiment

Cation	Ca	Na	La	Zn	Mg	Al	In
Ratio of ion charge to radius (e/Å)	1.15	0.63	1.79	1.57	1.45	2.38	2.05

Conclusion

8-Hydroxyquinoline chelate metal cation to form planar configuration that can decrease internal freedom degree of molecule, so that enhance probability of radiative transition. The effect of metal cation on π electrons in a large conjugate ring originates from the interaction of metal cation and solitary pair electrons to nitrogen atom. With the polarization force of cation increasing, the effect of cation on energy band enhances and all kinds of spectra present more and more red shift.

REFERENCES

1. Tang C.W., Vanslyke S.A. Organic electroluminescent diodes. Appl. Phy. Lett. 1987, Vol.51; 913: 915

2. Yuji H., Takeshi S., Masayuki F., Takanori F., Yoshitaka N., and Kenichi S. Organic Electroluminescent Devices with 8-Hydroxyquinoline Derivative Metal complexes as an Emitter. Jpn. J. Appl. Phy. 1993, Vol. 32; L514: L515

3. Akihiko F., Yutaka O., Chikayoshi M., and Katsumi Y. Photoluminescence Quenching under reverse Bias in Organic Multilayer structrue Utilizing 8-Hydroxyquinoline Aluminum and aromatic Diamine. Jpn. J. Appl. Phy. 1994, Vol. 33; L348 :L350

4. Guo Y.J. Fluorescence experimental Technology and Its Application in biology. Science Press. China, 1984

5. Prat M.D., Compano R., Beltran J.L. and Condony R. Fluorescence of Metal Complexes of 8-Hydroxyquinoline Derivatives in Aqueous Micellar Media. J. Fluorescence. 1994, Vol.4, No.4; 279: 281

6. Chen N.Y. Function of Bond's Parameter and It's Application (Chinese) Science Press , China, 1976

Received: January 3, 1996
Accepted: February 15, 1996