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Synthesis and photophysical properties of complexes of Be(II) and Zn(II) with 10-hydroxybenzo[*h*]quinoline ligand

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Abstract

Two 10-hydroxybenzo[*h*]quinoline metal complexes, bis(10-hydroxybenzo[*h*]quinolinato) beryllium ($Bebq_2$) and bis(10-hydroxybenzo[*h*]quinolinato)zincum ($Znbq_2$), have been synthesized. The structure are characterized by ^{1}HNMR, IR and so on. The photophysical processes of $Bebq_2$ and $Znbq_2$ have been carefully investigated by fluorescence spectra. The results show that the compounds emit yellow-green and yellow light. The emission peaks are at 492 and 512 nm, respectively. In addition, the light-emitting can be quenched by electron donor, *N*,*N*-dimethylaniline (DMA), and the quenching process follows the Stern–Volmer equation. Furthermore, the molecular interactions of $Bebq_2$ and $Znbq_2$ with electron acceptor, dimethylterephthalate (DMTP), were also carefully investigated. It displayed that the $Znbq_2$ is a potential substitute for $Bebq_2$ as an excellent emitting material.

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Keywords: 10-Hydroxybenzo[*h*]quinoline; Complexes; Interaction; *N*, *N*-Dimethylaniline; Dimethylterephthalate

1. Introduction

The design and fabrication of efficient organic light emitting devices (OLEDs) based on organic materials have been areas of active research due to their important applications in large area display technology. One of the most fascinating advantages in using these organic materials is a wide selection of emission colors in EL displays attainable through the molecular design of organic materials [1]. There have been extensive studies on organic EL devices using low molecular weight complexes with the aim of achieving high brightness, multicolor emission, and improving the durability and efficiency of devices [2,3]. Conventionally, Low molecular weight metal complexes, tris(8-hydroxyquinolinato)aluminum (Alq_3), has been considered to be the most excellent emitting material for organic EL devices. However, the 10-hydroxybenzo[*h*]quinoline beryllium complexes is superior to Alq_3 in EL character [4], and it has been achieved the standard of practical application. But, the toxicity of Beryllium made it impossible.

In this Paper, we have synthesized the bis(10-hydroxybenzo [*h*]quinolinato)beryllium ($Bebq_2$) and bis(10-hydroxybenzo [*h*]quinolinato)zincum ($Znbq_2$). The photophysical properties of $Bebq_2$ and $Znbq_2$ are investigated. The photoluminescence of $Bebq_2$ and $Znbq_2$ are examined in DMF. Moreover, the molecular interaction of with *N*,*N*-dimethylaniline (DMA) and dimethylterephthalate (DMTP) are investigated. Comparing their character, it displayed that the $Znbq_2$ is a potential substitute for $Bebq_2$ as an excellent emitting material.

2. Experimental

2.1. Materials and instruments

The reagents and chemicals for preparation of compounds were used as received unless noted otherwise. $BeSO_4{\cdot}4H_2O$, $ZnCl_2$, Ethanol, dichloromethane, dimethylterephthalate, ethyl acetate, *N*,*N*-dimethylaniline, petroleum ether, etc. were purchased from Beijing Chemical Plant and treated according to standard methods used before, which were all applied to measurement of the light-emitting properties. The synthetic route

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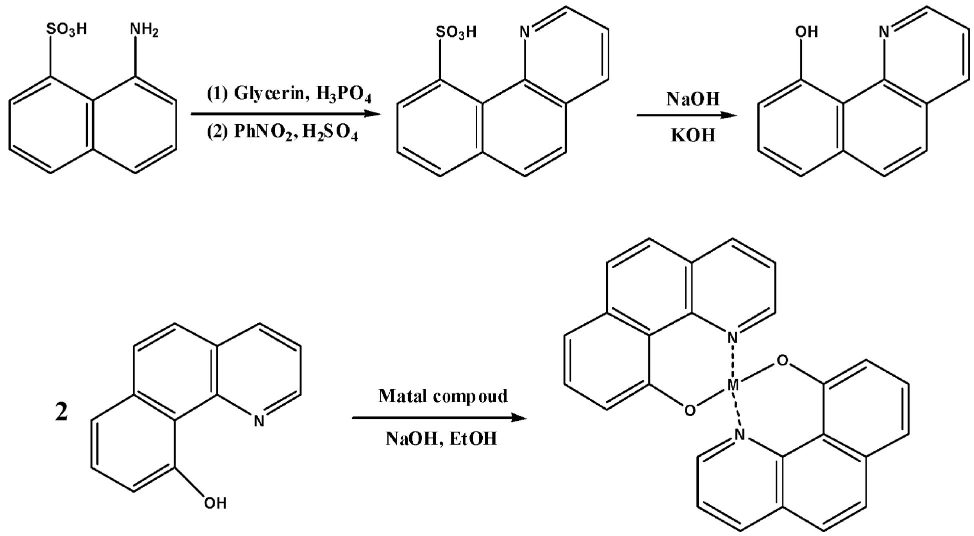

Scheme 1. The synthetic routes of compound.

used is shown in Scheme 1. Melting points were determined on a Sanyo Gallenkamp MPD350 melting point apparatus and uncorrected. The IR spectra were determined on a PE-1700 IR spectrophotometer by dispersing samples in KBr disks. ^{1}HNMR spectra were measured on a Bruker ARX300 spectrometer with $CDCl_3$ and DMSO as solvent. UV–vis and fluorescence spectra were obtained on a Shimadzu UV-265 spectrophotometer and Shimadzu RF-540 spectrofluorothotometer, respectively. Luminescence spectrometer was with a xenon lamp as the light source. Both excitation and emission bands were set at 5 and 2.5 nm, respectively. All the experiments were carried out at 20 ± 1 °C.

2.2. Preparation of materials

2.2.1. Preparation of 10-hydroxybenzo[h]quinoline

10-Hydroxybenzo[*h*]quinoline is prepared according to Ref. [5]. The yield is 70%, mp 101–102 °C, ^{1}HNMR ($DCCl_3$, ppm) δ: 14.947(1H), 8.842(1H), 8.279–8.257(1H), 7.837–7.809(1H), 7.657–7.637(3H), 7.442–7.420(1H), 7.274(1H); IR (KBr, cm^{-1}): 3461.9, 3433.1, 3398.3, 3049.3, 2686.7, 2617.2, 1622.0, 1581.5, 1527.5, 1465.8, 1407.9, 1388.7, 1332.7, 1269.1, 1203.5, 1126.4, 1060.8, 1018.3, 829.3, 757.9, 717.5, 676.9, 634.5, 567.0, 503.4.

2.2.2. Preparation of bis(10-hydroxybenzo[h]quinolinato)beryllium

10-Hydroxybenzo[*h*]quinoline (8 mmol) was dissolved in 40 ml of ethanol in a flask, $BeSO_4 \cdot 4H_2O$ (4 mmol) was dissolved in 100 ml of pure water in another flask, the 10-hydroxybenzo[*h*]quinoline solution was slowly poured into the $BeSO_4$ solution while stirring, $Bebq_2$ was deposited after the mixed solution was adjusted to pH 10 using NaOH, the $Bebq_2$ was filtered and purified by washing using ethanol. The yield is 90%, IR (KBr, cm^{-1}): 3433.1, 3047.3, 2927.7, 1625.9, 1581.5, 1519.8, 1433.1, 1409.9, 1332.7, 1299.9, 1280.6, 1215.1, 1174.6, 1141.8, 1078.1, 1041.5, 1016.4, 920.0, 891.1, 825.5, 800.4, 758.0, 736.8, 719.4, 650.0, 632.6, 569.0, 540.0, 511.1.

2.2.3. Preparation of bis(10-hydroxybenzo[h]quinolinato)zincum

10-Hydroxybenzo[*h*]quinoline (8 mmol) was dissolved in 40 ml of ethanol in a flask, $ZnCl_2$(4 mmol) was dissolved in 100 ml of pure water in another flask, the 10-hydroxybenzo[*h*]quinoline solution was slowly poured into the $ZnCl_2$ solution while stirring, $Znbq_2$ was deposited after the mixed solution was adjusted to pH 10 using NaOH, the $Znbq_2$ was filtered and purified by washing using ethanol. The yield is 93%, IR (KBr, cm^{-1}): 3440.8, 3047.3, 3020.3, 2923.9, 2852.52, 2688.6, 2578.7, 1623.9, 1577.7, 1529.5, 1469.7, 1433.0, 1413.7, 1392.5, 1334.65, 1271, 1139.9, 1027.9, 879.5, 829.3, 761.8, 717.5, 568.9 505.3, 449.4.

3. Results and discussion

3.1. ^{1}HNMR and IR of compounds

10-Hydroxybenzo[*h*]quinoline (HBQ) has very unique spectral properties. The fused 7,8-benzoquinoline structure constrains the O–H···N geometry of the dominant enol form to a nearly perfect six-membered ring hydrogen-bonding configuration. Thus, HBQ possesses a very strong hydrogen bond in the ground state, as indicated by a 14.9 ppm downfield-shifted hydroxyl proton (in $CDCl_3$) in the ^{1}H NMR study [6].

Comparing IR spectra of HBQ and $Bebq_2$ and $Znbq_2$. The absorption bands at 3462–3490 cm^{-1} forν(O–H) in the free ligand disappeared and new bands due toν(M–O) appeared in the regions 1433.0 cm^{-1}. The band of 1269.1 cm^{-1} ν(C=N) has red shift to 1271.0 and 1299.9 cm^{-1} is due to the conjugation of the p-orbital on the double bond with the d-orbital on metal ion with reduction of the force constant [7]. The new absorption band at 3433–3047 cm^{-1} in the complexes can be assigned to hydroxyl stretching vibration of the crystal water involved in the complexes. In the far IR region two new bands around 511.1–540.0 and 449.4–503.4 cm^{-1} in the complexes can be assigned toν(M–O) andν(M–N), respectively.

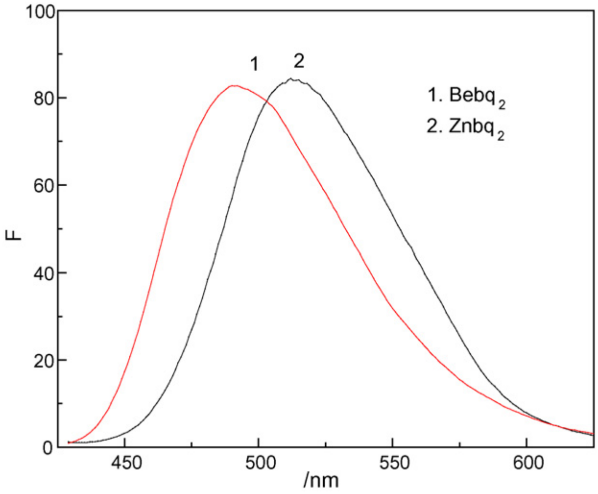

Fig. 1. The fluorescence spectra of Bebq$_2$ and Znbq$_2$ in DMF.

3.2. Fluorescence emission spectra

The fluorescence emission spectra of Bebq$_2$ and Znbq$_2$ in DMF are shown in Fig. 1. It can be seen from Fig. 1. that the maximum emission peaks are at 492 and 512 nm, respectively. This shows that the Bebq$_2$ and Znbq$_2$ emit yellow-green and yellow light and are desirable emitting photoluminescence material, respectively.

3.3. Interaction of Bebq$_2$ and Znbq$_2$ with N, N-dimethylaniline

N,*N*-Dimethylaniline is a typical electron donor [8]. The studies of interactions between metal complexes and DMA are helpful to understanding the photo-electronic properties of metal complexes. So the quenching process of Bebq$_2$ and Znbq$_2$ with DMA is examined. With the gradual increase in concentration of DMA, the fluorescence of Bebq$_2$ and Znbq$_2$ are all quenched efficiently and the processes also follow the Stern–Volmer equation (Figs. 2 and 3). The apparent quenching constants are $4.98 \times 10^1\ M^{-1}$ and $7.04 \times 10^2\ M^{-1}$, respectively. Which suggests that the strong interactions between two metal complexes and DMA happen in the excited state.

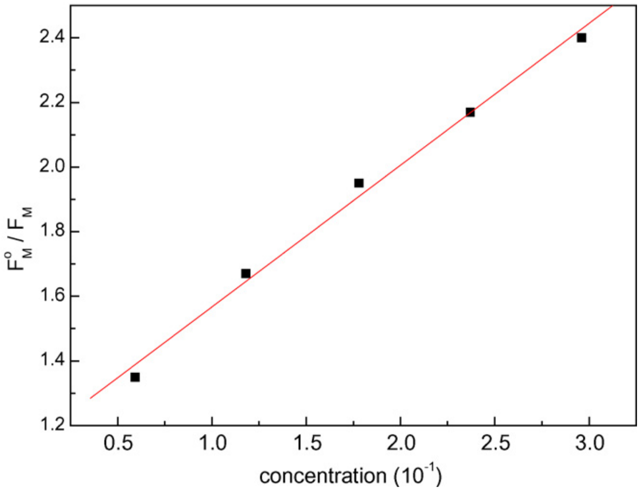

Fig. 2. Dependence of F^O_M/F_M on concentration of DMA. Concentration of Bebq$_2$, 5.0×10^{-5} M.

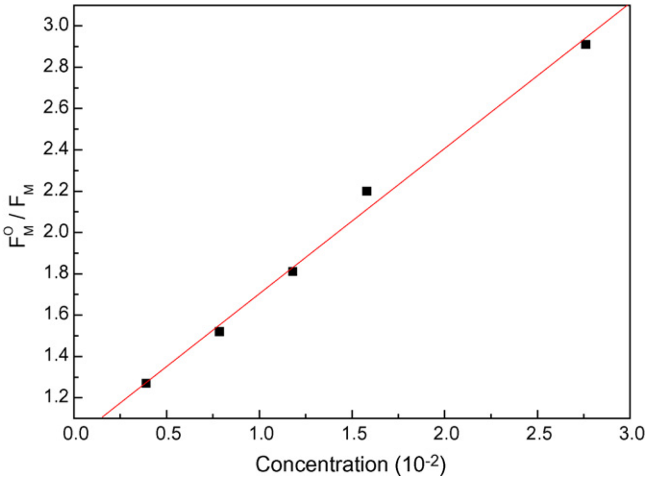

Fig. 3. Dependence of F^O_M/F_M on concentration of DMA. Concentration of Znbq$_2$, 1.25×10^{-5} M.

3.4. Interaction of Bebq$_2$ and Znbq$_2$ with dimethylterephthalate

In this paper, the interactions between two metal complexes and DMTP are investigated, DMTP is a typical electron acceptor [9], which is helpful to understand the optical property of Bebq$_2$ and Znbq$_2$ and apply it to OLED. The experiments show that the fluorescence of Bebq$_2$ is initially increased and then decreased with gradual increasing in concentration of DMTP in DMF, furthermore, the interactions are not distinct and shown in Fig. 4. However, It can be seen from Fig. 5 that the fluorescence of Znbq$_2$ is quenched efficiently and the processes also follow the Stern–Volmer equation. The apparent quenching constant are $4.63 \times 10^3\ M^{-1}$. This can be explained by the following reasons:

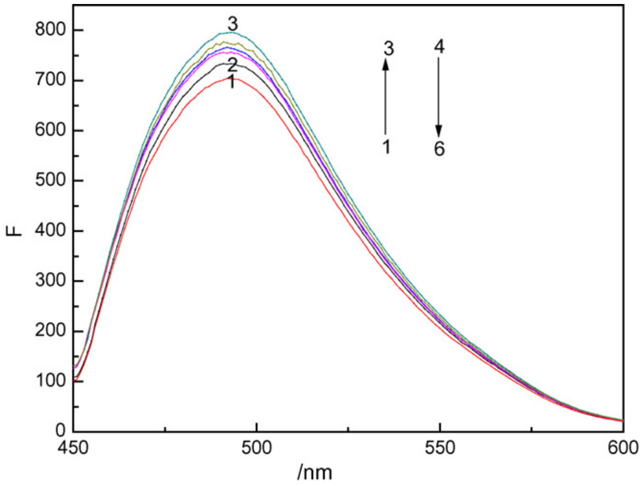

Fig. 4. Fluorescence spectra of Bebq$_2$ at different concentrations of DMTP. Concentration of Bebq$_2$, 1.25×10^{-5} M. Concentration of DMTP (mol/l, M); (1) 0.00; (2) 5×10^{-5}; (3) 2×10^{-4}; (4) 3.5×10^{-4}; (5) 7×10^{-4}; (6) 9.5×10^{-4}.

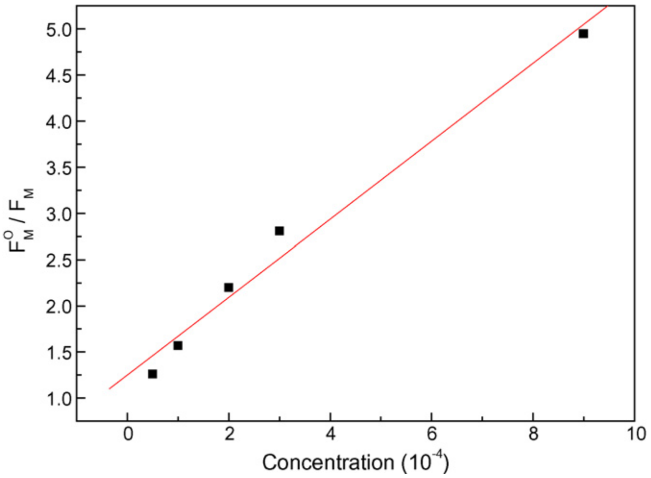

Fig. 5. Dependence of $F_{\mathrm{M}}^{\mathrm{O}}/F_{\mathrm{M}}$ on concentration of DMTP. Concentration of Znbq$_2$, 1.25×10^{-5} M.

the carrier transport capability of Znbq$_2$ may be superior to that of Bebq$_2$, and the Znbq$_2$ is a potential substitute for Bebq$_2$ as an excellent emitting material. Further research towards a better understanding of this difference is currently in progress.

4. Conclusions

In summary, two 10-hydroxybenzo[*h*]quinoline metal complexes, bis(10-hydroxybenzo[*h*]quinolinato)beryllium (Bebq$_2$) and bis(10-hydroxybenzo[*h*]quinolinato)zincum (Znbq$_2$), have been synthesized. The photophysical processes of Bebq$_2$ and Znbq$_2$ have been carefully investigated by fluorescence spectra. The results show that the compounds emit yellow-green and yellow light. The emission peaks are at 492 and 512 nm, respectively. In addition, the light-emitting can be quenched by electron donor, *N*,*N*-dimethylaniline, and the quenching process follows the Stern–Volmer equation. Furthermore, the molecular interactions of Bebq$_2$ and Znbq$_2$ with electron acceptor, dimethylterephthalate, were also carefully investigated. It displayed that the Znbq$_2$ is a potential substitute for Bebq$_2$ as an excellent emitting material.

Acknowledgements

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