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Synthesis and photophysics of novel 8-hydroxyquinoline aluminum metal complex with 1,3,4-oxadiazole units

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Abstract

A novel luminescent metal complex, $(OXHQ)_3AI$, with 8-hydroxyquinoline aluminum and electron-transporting 1,3,4-oxadiazole unit was designed and synthesized. The photophysical processes were investigated by UV–vis absorption and fluorescence emission spectra in diluent solution. The results showed that the luminescence quantum yield of $(OXHQ)_3AI$ was 0.67 in DMSO and it emitted blue light with the band gap of 3.13 eV estimated from the onset absorption. In addition, the light-emitting of $(OXHQ)_3AI$ can be quenched by electron acceptor (dimethylterephalate), where the processes followed the Stern–Volmer equation. However, with the addition of electron donor (N,N-dimethylaniline) fluorescent intensity of $(OXHQ)_3AI$ was increased and emission peak was lightly blue-shift. Furthermore, the molecular interactions of $(OXHQ)_3AI$ with fullerene (C_{60}) or carbon nanotubes (CNTs) were also carefully investigated.

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1. Introduction

Organic light-emitting diodes (LEDs) based on electroluminescence (EL) of conjugated polymers and molecular materials have attracted great attention during the past decade because of their potential applications in a new generation of display and lighting technologies [1-3]. However, there are still many important and fundamental challenges remain, such as quantum efficiency, purer colors, emission wide etc., especially, including the carrier transfer ratio. It is well known that to achieve good performance in LEDs the injection of electrons and transport of holes should be balanced. In addition, the luminance efficiency of the device determined by the amount of charge carrier injection, the probability of the capture of charges, and the ratio of singlet excitons formed is limited [4,5]. A balance of the rates of injection of electrons and holes from opposite contacts into the device is crucial in achieving high electroluminescent efficiency [6-8].

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In order to improve the photoluminescent efficiency, many strategies have been used including multilayer devices, a blend of electron transport material with EL compound etc. However, these are unavoidable drawbacks to the approaches. The optimization method to improve the performance of LEDs is that introduced electron transport moieties into the main luminophor [9-11]. Several 1,3,4-oxadiazole (OXD) derivatives, such as 2-(4'-biphenylyl)-5-(4'-tert-butylphenyl)-1,3,4-oxadiazole (PBD) have been actually used as electron-injection materials to improve the balance of charge carrier and to increase the photon/electron quantum efficiency [12,13]. 8-Hydroxyquinoline is one of the most important chelators for metal ions and has found significant applications in a variety of investigations involving metal complexes. 8-hydroxyquinoline aluminum has been widely used as the emissive and electron transporting material in organic light-emitting devices (OLEDs) [14,15].

In the paper, we designed and synthesized a new metal complex, (OXHQ)₃Al, with 8-hydroxyquinoline aluminum and electron-injecting oxadiazole moieties, in order to improve the transporting performance of 8-hydroxyquinoline aluminum. The photophysical processes were investigated by UV–vis absorption and fluorescence emission spectra. Additionally, the interactions of (OXHQ)₃Al and electron donor or electron

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Scheme 1. The synthetic route of (OXHQ)₃Al.

acceptor have been carefully studied. Moreover, the molecular interactions of $(OXHQ)_3AI$ with fullerene (C_{60}) or carbon nanotubes (CNTs) were also investigated. The results show that the metal complex $(OXHQ)_3AI$ is emitting blue light material compound.

2. Experimental

2.1. Materials and instruments

The reagents and chemicals for preparation of ligand and complex were used as received unless noted otherwise. Ethanol, dichloromethane, toluene, chloroform, ethyl acetate, DMSO, 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 synthesis route used was 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. ¹H NMR spectra were measured on a Bruker ARX300 spectrometer with DMSO as solvent. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.) UV–vis and fluorescence spectra were obtained on a Shimadzu UV-265 spectrophotometer and Shimadzu RF-540 spectrofluorothotometer, respectively. Luminescence spectrometer was measured with a xenon lamp as the light source. Both excitation and emission bands were set at 10. All the experiments were carried out at room temperature.

2.2. Synthesis

2.2.1. 5-Chloromethyl-8-hydroxyquinoline hydrochloride

A mixture of 7.3 g (0.05 mol) 8-hydroxyquinoline, 10 ml of cond. Hydrochloride acid, and 8 ml (0.05 mol) of 37% formald-edyde was treated with hydrogen chloride gas for 90 min. The yellow solid was collected on a filter and dried to give 8.9 g (77.5% yield), m.p. 280 °C (lit m.p. 283 °C).

2.2.2. 5-[4-(5-Phenyl-1,3,4-oxadiazol-2-yl) phenylamino]methyl-8-hydroxyquinolinel (OXHQ)

A mixture of 7.88 g (0.02 mol) 2-phenyl-5-(4'-amine)phenyl-1,3,4-oxadiazole, 1.08 g (0.02 mol) CH₃ONa, 30 ml DMSO and 1.12 g (0.02 mol) KOH was stirred at room temperature for 2 h. 4.6 g (0.02 mol) 5-chloromethyl-8-hydroxyquinoline hydrochloride, which was dissolved by 20 ml DMSO, was slowly dropped into the above solution. The mixture was stirred at room temperature for 10 h and heated to 70 °C for 2 h. The reaction solution was filtrated after adding to 200 ml water and neutralizing by 10% hydrochloric acid solution, the precipitate was dissolved by ethanol, then adding the ethanol solution to



Fig. 1. The UV–vis absorption and fluorescent emission spectra of (OXHQ)_3Al (3.18 \times 10 $^{-5}$ M) in DMSO.

100 ml ice water gave the crude product. The crude product was purified by silica gel column chromatography (eluent: ethyl acetate: *n*-hexane = 6:1). Yield: 52.3%. IR (KBr pellet) cm⁻¹: 3401, 1652, 1590, 1562, 1495, 1145, 783; ¹H-NMR (*d*-DMSO): δ : 8.92 (s, 1H), 8.54 (s, 1H), 7.61–6.94 (m,11H), 4.73 (s, 2H), 4.32 (s, 1H). Element Anal. Calcd for OXHQ (C₂₄H₁₈N₄O₂): C, 73.08; H, 4.60; N, 14.20; Found: C, 72.88; H, 4.63; N, 14.55.

2.3. (OXHQ)₃Al

A 10 ml solution with 0.002 mol AlCl₃, 3.0 ml methanol, 7.0 ml dichloromethane was slowly added to dissolved 0.002 mol 5-[4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenylamino)]methyl-8-hydroxyquinolinel (OXHQ) dichloromethane solution at refluxing. The reaction system was refluxed for 30 min and appeared a lot deposition. After filtrating, washing and drying, the (OXHQ)₃Al metal complex was obtained m.p. > 300 °C.

3. Results and discussion

3.1. UV-vis absorption and fluorescence emission spectrum

Fig. 1 showed the UV–vis absorption and fluorescence emission spectra of (OXHQ)₃Al in dilute DMSO solution. The UV–vis absorption spectra of (OXHQ)₃Al was 342 nm, which should mainly come from 8-hydroxyquinoline unit absorption. However, the fluorescence emission peak of (OXHQ)₃Al was 455 nm that showed obviously blue-shift comparing to that of 8-hydroxyquinoline aluminum. It was due to 1,3,4-oxadiazole (OXD) ring properties that was an electron deficient group and had big electron affinity, the charge transfer process of 8-hydroxyquinoline aluminum to 1,3,4-oxadiazole unit would weaken the conjugated extent of metal complex, so the emission peak of (OXHQ)₃Al was obviously blue-shift comparing to that of 8-hydroxyquinoline aluminum.

3.2. Quantum yield of photoluminescence and the band gap

The fluorescence quantum yield was measured by relative method using the quinine sulfate as the standard (0.546 in $0.5 \text{ mol } L^{-1} \text{ H}_2 \text{SO}_4$) [16]. The quantum yield is calculated from

the following equation:

$$\Phi_{\rm s} = \Phi_{\rm r} \frac{F_{\rm S}}{F_{\rm r}} \frac{A_{\rm r}}{A_{\rm s}} \left(\frac{n_{\rm r}}{n_{\rm s}}\right)^2$$

In the above expression, Φ_s is the fluorescent quantum yield, *F* is the integration of the emission intensities, *n* is the index of refraction of the solution, and *A* is the absorbance of the solution at the exciting wavelength. The subscripts r and s denote the reference and unknown samples, respectively. The value of quantum yield of (OXHQ)₃Al in DMSO was 0.67. The band gap (E_g^{opt}) of the complex can be estimated from the onset absorption (UV_{onset}) with E_g^{opt} (eV) = hc/λ (h = 6.626 × 10⁻³⁴ J s, c = 3 × 10¹⁷ nm/s, 1eV = 1.602 × 10⁻¹⁹ J). The band gap of the metal complex was 3.13 eV.

3.3. The interactions of (OXHQ)₃Al with dimethylterephalate (DMTP) and N,N-dimethylaniline (DMA)

The fluorescence quenching technique was a helpful method for the study of the mechanism of molecular interaction, energy transfer or charge transfer. Dimethylterephalate (DMTP) was a typical electron acceptor and N,N-dimethylaniline (DMA) was a typical electron donor. When DMTP was added to a solution of (OXHQ)₃Al in DMSO, the fluorescence of (OXHQ)₃Al was efficiently quenched and the quenching process followed the Stern-Volmer equation. The apparent quenching coefficient, $K_{\rm sv}$, was $2.37 \times 10^4 \,{\rm M}^{-1}$ (as shown in Fig. 2). The quenching process of (OXHQ)₃Al with DMA was also examined and shown in Fig. 3. It can be seen that the emission intensity of fluorescence were lightly decreased and the emission peaks were obviously blue-shift with gradual increasing in concentration of DMA in DMSO, which was obviously distinct phenomenon with DMTP. From the experimental facts and references, an explanation was proposed: N.N-dimethylaniline (DMA) was a rich electron group with stronger ligand capability, so the interaction between metal and ligands would be weakened with the addition of DMA, which would result in the emission spec-



Fig. 2. Fluorescence spectra of (OXHQ)₃Al at different concentration of DMTP. Concentration of (OXHQ)₃Al, 3.18×10^{-5} M; concentration of DMTP (mol/L, M), 0,0.00; 1, 6.52×10^{-7} ; 2, 1.06×10^{-6} ; 3, 4.78×10^{-6} ; 4, 9.24×10^{-6} ; 5, 2.07×10^{-5} ; 6, 7.88×10^{-5} .



Fig. 3. Fluorescence spectra of $(OXHQ)_3Al$ at different concentration of DMA. Concentration of $(OXHQ)_3Al$, 3.18×10^{-5} M; Concentration of DMA (mol/L, M), 0, 0.00; 1, 6.62×10^{-6} ; 2, 2.34×10^{-6} ; 3, 1.02×10^{-5} ; 4, 6.69×10^{-5} ; 5, 2.28×10^{-4} ; 6, 4.96×10^{-4} ; 7, 8.73×10^{-4} ; 8, 4.85×10^{-3} .

tra blue-shift. In addition, 1,3,4-oxadiazole (OXD) ring was an electron deficient group and had big electron affinity, the electron transfer processes of DMA to OXD would decrease the fluorescent intensity of (OXHQ)₃Al metal complex.

3.4. Interaction between $(OXHQ)_3Al$ and fullerene (C_{60})

Many researches show C_{60} bears many unusual electrochemical and electronic properties. One of the most remarkable properties of C_{60} related to electron transfer phenomena is that it can efficiently induce a rapid charge separation and a further slow charge recombination [17]. In the experiment, the interactions of (OXHQ)₃Al with C_{60} were examined. The results were shown in Fig. 4. As we have seen in Fig. 4, '0' was (OXHQ)₃Al in concentration (3.18 × 10⁻⁵ M) without C_{60} , '1–7' were (OXHQ)₃Al in the present in different concentration of C_{60} . With the gradual increasing of concentration of C_{60} , the fluorescence of (OXHQ)₃Al was quenched efficiently and the process was also following the Stern–Volmer equation (Fig. 5). The apparent quenching constant was $1.33 \times 10^4 \text{ M}^{-1}$, which suggests that the strong interactions between (OXHQ)₃Al







Fig. 5. Dependence of F^0/F on the concentration of C₆₀. [(OXHQ)₃Al]: 3.18×10^{-5} M.

and C_{60} happen in the excited state. This can be explained by two reasons. Firstly, both (OXHQ)₃Al and C_{60} have a large π conjugated system in which π - π interaction may change the configuration of (OXHQ)₃Al [18]. Secondly, the photo-induced charge transfer from excited (OXHQ)₃Al to C_{60} was rapid. Upon this charge transfer the conjugated system may be dramatically modified and distorted because of the strong electron–lattice interaction in the one-dimensional system [19].

3.5. Interaction between (OXHQ)₃Al and carbon nanotubes (CNTs)

The investigation on the interaction between (OXHQ)₃Al and carbon nanotubes (CNTs) was helpful to understand the optical property of (OXHQ)₃Al and apply it to LEDs. The interaction between them in diluted solutions is examined by fluorescence spectrophotometry and the results indicate that the fluorescence of (OXHQ)₃Al can be quenched by carbon nanotubes (Fig. 6). It can be seen that the emission intensities of fluorescence are decreased with gradual increasing in concentration of CNTs in DMSO. Meantime, the emission peaks had no obvious change. The phenomenon indicated that the intense



Fig. 6. Fluorescent spectra of (OXHQ)₃Al at different concentration of CNTs. Concentration of (OXHQ)₃Al, 3.18×10^{-5} M; concentration of CNTs (mg mL⁻¹), 0, 0.00; 1, 4.26×10^{-6} ; 2, 7.84×10^{-6} ; 3, 9.87×10^{-6} ; $4,2.98 \times 10^{-5}$; 5, 6.13×10^{-5} .

interaction of (OXHQ)₃Al and CNTs in excited state was happened [20,21]. Further research toward a better understanding of this action is currently in progress.

4. Conclusions

A novel metal complex $(OXHQ)_3$ Al containing excellently luminescent capability groups, 8-hydroxyquinoline aluminum and electron transport units was designed and synthesized. The photophysical properties research showed the absorption peak was 342 nm and the emission was located 455 nm in DMSO. The luminescence quantum yield was 0.67 in DMSO. The lightemitting can be quenched by electron acceptor and the quenched processes followed the Stern–Volmer equation, the molecular interactions of $(OXHQ)_3$ Al with fullerene (C₆₀) or carbon nanotubes happened in the excited state. It can be anticipated that the metal complex will have a potential application as an emitting blue light material.

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References

 J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, A.B. Holmes, Nature 347 (1990) 539.

- [2] C.W. Tang, S.A. VanSlyke, Appl. Phys. Lett. 51 (1987) 913.
- [3] C.S. Wang, G.Y. Jung, Y.L. Hua, C. Pearson, M.R. Bryce, M.C. Petty, A.S. Batsanov, A.E. Goeta, J.A.K. Howard, Chem. Mater. 13 (2001) 1167.
- [4] D.W. Lee, K. YKwon, J.I. Jin, Y.S. Park, Y.R. Kim, I.W. Hwang, Chem. Mater. 13 (2001) 565.
- [5] Y.Z. Lee, X. Chen, S.A. Chen, P.K. Wei, W.S. Fann, J. Am. Chem. Soc. 123 (2001) 2296.
- [6] S.C. Greenham, S.C. Moratti, D.D.C. Bradley, R.H. Friend, A.B. Holmes, Nature 365 (1993) 628.
- [7] F. Garten, A. Hilberer, F. Cacialli, E. Essenlink, Y. van Dam, B. Schlatmann, R.H. Friend, T.M. Klapwijk, G. Hadziioannou, Adv. Mater. 9 (1997) 127.
- [8] S.H. Jin, M.Y. Kim, J.Y. Kim, K. Lee, Y.S. Gal, J. Am. Chem. Soc. 126 (2004) 2474.
- [9] S.Y. Song, M.S. Jang, H.K. Shim, D.H. Hwang, T. Zyung, Macromolecules 32 (1999) 1482.
- [10] S.H. Jin, H.J. Park, J.Y. Kim, K. Lee, S.P. Lee, D.K. Moon, H.J. Lee, Y.S. Gal, Macromolecules 35 (2002) 7532.
- [11] S.H. Jin, S.Y. Kang, M.Y. Kim, U.C. Yoon, J.Y. Kim, K.H. Lee, Y.S. Gal, Macromolecules 36 (2003) 3841.
- [12] C. Zhang, H. von Seggern, K. Pakbaz, B. Kraabel, H.W. Schmidt, A.J. Heeger, Synth. Met. 62 (1994) 35.
- [13] Y.Q. Liu, X.Z. Jiang, Q.L. Li, D.B. Zhu, Synth. Met. 4 (1997) 36.
- [14] H.D. Burrows, M. Fernandes, J. Seixas de Melo, A.P. Monkman, S. Navaratnam, J. Am. Chem. Soc. 125 (2003) 15310.
- [15] G.M. Credo, D.L. Winn, S.K. Buratto, Chem. Mater. 13 (2001) 1258.
- [16] J.N. Dmas, G.A. Crobys, J. Phys. Chem. 71 (1971) 991.
- [17] B.W. Jing, D.Q. Zhang, D.B. Zhu, Tetrahedron Lett. 41 (2000) 8559.
- [18] S.H. Gallagher, R.S. Armstrong, P.A. Lay, C.A. Reed, J. Phys. Chem. 99 (1995) 5817.
- [19] S. Morita, A.A. Zakhidov, K. Yoshino, Solid State Commun. 82 (1992) 249.
- [20] S. Iijima, Nature (London) 354 (1991) 56.
- [21] R. Saito, G. Dresselhaus, M.S. Dresselhaus, Physical Properties of Carbon Nanotubes, Imperial College Press, London, 1998.