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Synthesis and photophysics of novel 8-hydroxyquinoline aluminum metal dye with hole transfer groups

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ABSTRACT

A novel luminescent dye metal complex, $(CZHQ)_3Al$, with 8-hydroxyquinoline aluminum and holetransporting carbazole units was designed and synthesized. The $(CZHQ)_3Al$ optical properties were carefully investigated by UV-vis absorption and fluorescence spectra in diluent solution. The results showed that the luminescent quantum yield of $(CZHQ)_3Al$ was 0.62 in DMSO and it emitted red-light with the band gap of 2.89 eV estimated from the onset absorption. In addition, the light-emission of $(CZHQ)_3Al$ can be quenched by electron acceptor (dimethylterephalate), where the process followed the Stern–Volmer equation. However, the fluorescent intensities of $(CZHQ)_3Al$ were slowly increased with the addition of electron donor (*N*,*N*-dimethylaniline). Furthermore, the molecular interactions of $(CZHQ)_3Al$ with fullerene (C_{60}) and carbon nanotubes (CNTs) were also respectively investigated, which indicated the metal dye can be used as new fluorescent probe.

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1. Introduction

Recently, the field of research about photoluminescent (PL) and electroluminescent (EL) materials is growing rapidly due to the versatility and practical applications of these compounds. Especially, photoluminescent and electroluminescent devices based on organic thin layers have attracted much attention because of the potential application to large-area flat-panel displays and lightemitting diodes (LEDs) [1,2].

Much progress has been made in recent years to improve the efficiencies of the EL devices through ingenious device configurations, electrode modification, and new material discoveries [3–5]. Numerous fluorescent dyes and charge carriers have been developed, yet the efforts are still going on in terms of color tuning, higher efficiency, and durability. Low LE efficiency in LEDs is attributed mainly to an imbalance in the transportation rates of the electrons and holes in LE layers [6–9]. To overcome the problem of low LE efficiency, it is urgent and perfect for combining the electron-injecting group, hole-transporting group and chromophore in the same molecule. Carbazole and its derivatives are good hole-transport materials and have been used in construction of light-emitting device (LEDs) [10–13]. 8-Hydroxyquinoline is one of the most important chelators for metal ions and has found sig-

nificant applications in a variety of investigations involving metal complexes. 8-Hydroxyquinoline aluminum (Alq₃) has been widely used as the emissive and electron-transporting material in organic light-emitting devices (OLEDs) [14–16]. On the aspect, Professor H. Tian et al. successfully obtained multifunctional material compound of hole-transporting group and Alq₃ by large π -conjugated system [17]. However, it is well known that the excellent luminescent material properties, such as efficiency, brightness, plasticity, lie on discontinuous π -conjugated system on the extent.

Herein, in order to improve the transporting performance of 8hydroxyquinoline aluminum, we designed and synthesized a new metal complex, $(CZHQ)_3Al$, with 8-hydroxyquinoline aluminum and hole-transporting carbazole groups. The optical properties were investigated by UV–vis absorption and fluorescence emission spectra. Additionally, the interactions of $(CZHQ)_3Al$ with electron donor or electron acceptor have been carefully studied. Moreover, the molecular interactions of $(CZHQ)_3Al$ with excellent semiconductor materials, such as fullerene (C_{60}) and carbon nanotubes (CNTs), were also carefully investigated. The results show that the metal complex $(CZHQ)_3Al$ can emit red-light.

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,

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

dichloromethane, toluene, chloroform, ethyl acetate, DMSO, petroleum ether, etc. were purchased from Beijing Chemical Plant and treated according to standard methods before use, which were all applied to measurement of the light-emitting properties. The synthesis route used was shown in Scheme 1.



Fig. 1. The UV-vis absorption spectra of $(CZHQ)_3Al (5.24 \times 10^{-5} \text{ M})$ in DMSO.

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 solvents. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementary Co.) UV–vis absorption and fluorescence spectra were obtained on a Shimadzu UV-265 spectrophotometer and Shimadzu RF-540 spectrofluorophotometer, respectively. Luminescence spectrometer was measured with a xenon lamp as the light source. Both excitation and emission bands were set at 10 nm. 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 36.5% hydrochloride acid and 8 ml (0.05 mol) of 37% formaldehyde 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-[(Carbazol-9'-yl)methyl]-8-hydroxyquinoline (CZHQ)

A mixture of 3.34 g (0.02 mol) carbazole, 0.6 g (0.025 mol) NaH and 30 ml DMSO was stirred until no bubble generated at room temperature. After filtering the mixture, 1.12 g (0.02 mol) KOH was added to the solution. 4.6g (0.02 mol) 5-Chloromethyl-8hydroxyquinoline hydrochloride, which was dissolved by 10 ml DMSO, was slowly dropped into the above solution. The mixture was stirred at room temperature for 3 h and heated to 70 °C for 2 h. The reaction solution was filtrated after adding to 200 ml water, the precipitate was dissolved by ethanol, then adding the ethanol solution to 100 ml ice water gave the crude product. The crude product was purified by silica gel column chromatography (eluent: ethyl acetate:*n*-hexane = 1:4). Yield: 51.8%. IR (KBr pellet) cm^{-1} : 3050, 1660, 1590, 1575, 1530, 1170, 795; ¹H NMR (*d*-DMSO): δ 8.88 (s, 1H), 8.22 (s, 1H), 7.52-6.87 (m, 11H), 5.95 (m, 2H). Element Anal. Calcd. for CZHQ (C₂₂H₁₆N₂O): C, 81.46; H, 4.97; N, 8.64. Found: C, 81.52: H. 5.13: N. 8.55.

2.2.3. (CZHQ)3Al

A mixture of 0.002 mol AlCl₃, 3.0 ml methanol, 7.0 ml dichloromethane was slowly added to 30 ml dichloromethane under refluxing which was dissolved in 0.002 mol 5-((9H-carbazol-9-yl)methyl)-8-hydroxyquinoline (CZHQ). The reaction mixture was refluxed for 30 min and a lot of deposition appeared. After filtrating, washing and drying, the (CZHQ)₃Al metal complex was obtained (m.p. >300 °C).

3. Results and discussion

3.1. UV-vis absorption and fluorescence emission spectrum

Fig. 1 shows the UV–vis absorption spectra of (CZHQ)₃Al in dilute DMSO solution. The maximum UV–vis absorption peak of CZHQ was 343 nm with shoulder peak 330 nm, which was similar with the absorption spectra of carbazole and it should mainly come from carbazole unit absorption. However, the fluorescence emission peak of (CZHQ)₃Al was 522 nm that rooted in the emission peak of 8-hydroxyquinoline aluminum. In addition, due to the charge transfer process of hole-transfer group (carbazole) and electron-transfer group (8-hydroxyquinoline), the maximum emission peak of (CZHQ)₃Al was obviously red-shift comparing to that of 8-hydroxyquinoline aluminum.

3.2. Quantum yield of photoluminescence and the band gap

The photoluminescent quantum yield of $(CZHQ)_3Al$ was measured by relative method using the quinine sulfate as the standard $(0.546 \text{ in } 0.5 \text{ mol}/l \text{ H}_2\text{SO}_4)$ [18]. The quantum yield was 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 (CZHQ)₃Al in DMSO was 0.62. The band gap (E_g^{opt}) of the complex can be estimated from the onset absorption (UV_{onset}) with $E_g^{opt}(eV) = hc/\lambda$ ($h = 6.626 \times 10^{-34}$ Js, $c = 3 \times 10^{17}$ nm/s, $1 \text{ eV} = 1.602 \times 10^{-19}$ J). The band gap of the metal complex was 2.89 eV.



Fig. 2. Fluorescence spectra of $(CZHQ)_3Al$ at different concentration of DMTP. Concentration of $(CZHQ)_3Al$, 5.24×10^{-5} M; concentration of DMTP (mol/l, M), 0, 0.00; 1, 7.33×10^{-7} ; 2, 2.16×10^{-6} ; 3, 5.12×10^{-6} ; 4, 9.44×10^{-6} ; 5, 2.87×10^{-5} ; 6, 8.14×10^{-5} .

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

The fluorescence quenching technique was a helpful method for the study of the mechanism of molecular interaction, energy transfer or charge transfer. Dimethylterephthalate (DMTP) was a typical electron acceptor and N,N-dimethylaniline (DMA) was a typical electron donor. When DMTP was added to a solution of (CZHQ)₃Al in DMSO, the fluorescence of (CZHQ)₃Al was efficiently quenched and the quenching process followed the Stern-Volmer equation (as shown in Fig. 2). The apparent quenching coefficient, $K_{\rm sv}$, was 1.54×10^4 M⁻¹. The quenching process of (CZHQ)₃Al with DMA was also examined and shown in Fig. 3. It can be seen that the fluorescence emission intensity of (CZHQ)₃Al were increased with gradual addition of DMA in DMSO, which was obviously different phenomenon with DMTP adding to (CZHQ)₃Al solution. From the experimental facts and references, an explanation is possible reasonable: DMA is a rich electron group with stronger ligand capability. There are competitive complex processes with metal Al³⁺ and ligand atoms or molecules from DMA and CZHQ when DMA is gradually added into the (CZHQ)₃Al solution. The action of DMA and Al³⁺ can reduce the quenching fluorescent intensities of (CZHQ)₃Al from metal Al³⁺ ions.



Fig. 3. Fluorescence spectra of $(CZHQ)_3Al$ at different concentration of DMA. Concentration of $(CZHQ)_3Al$, 5.24×10^{-5} M; concentration of DMA (mol/l, M), 0, 0.00; 1, 5.78×10^{-6} ; 2, 1.97×10^{-6} ; 3, 9.88×10^{-6} ; 4, 1.16×10^{-5} ; 5, 2.28×10^{-5} ; 6, 4.96×10^{-5} ; 7, 7.83×10^{-4} .



Fig. 4. Fluorescent spectra of (CZHQ)₃Al at different concentration of C₆₀. Concentration of (CZHQ)₃Al, 5.24×10^{-5} M; concentration of C₆₀ (mol/l, M), 0, 0.00; 1, 4.36×10^{-6} ; 2, 1.27×10^{-5} ; 3, 2.87×10^{-5} ; 4, 3.41×10^{-5} ; 5, 6.11×10^{-5} ; 6, 1.31×10^{-4} ; 7, 1.76×10^{-4} .

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

Many researches show C₆₀ bears many unusual electrochemical and electronic properties. One of the most remarkable properties of C₆₀ related to electron transfer phenomena is that it can efficiently induce a rapid charge separation and a further slow charge recombination [19]. In the experiment, the interactions of (CZHQ)₃Al with C₆₀ were examined. It can be seen in Fig. 4, '0' was $(CZHQ)_3Al (5.24 \times 10^{-5} \text{ M})$ without C_{60} , '1-7' were $(CZHQ)_3Al$ in the present in different concentration of C_{60} . With gradual increase in the concentration of C₆₀, the fluorescence of (CZHQ)₃Al was quenched efficiently and the process was also following the Stern-Volmer equation (Fig. 5). The apparent quenching constant was $1.19\times 10^4\,M^{-1}$, which indicated the strong interactions between $(CZHQ)_3Al$ and C_{60} in the excited state had happened. This can be explained by two reasons. Firstly, both $(CZHQ)_3$ Al and C₆₀ had a large π -conjugated system in which π - π interaction may change the configuration of (CZHQ)₃Al [20]. Secondly, the photo-induced charge transfer from excited (CZHQ)₃Al to C₆₀ 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 [21].



Fig. 5. Dependence of F_0/F on the concentration of C_{60} . [(CZHQ)₃Al]: 5.24×10^{-5} M.



Fig. 6. Fluorescent spectra of $(CZHQ)_3Al$ at different concentration of CNTs. Concentration of $(CZHQ)_3Al$, 5.24×10^{-5} M; concentration of CNTs (mg ml⁻¹), 0, 0.00; 1, 5.36×10^{-6} ; 2, 8.21×10^{-6} ; 3, 9.67×10^{-6} ; 4, 3.08×10^{-5} ; 5, 7.23×10^{-5} .

3.5. Interaction between (CZHQ)₃Al and carbon nanotubes

The investigation on the interaction between $(CZHQ)_3AI$ and CNTs was helpful to understand the optical property of $(CZHQ)_3AI$ and apply it to LEDs. The interaction between them in diluted solutions was examined by fluorescence spectrophotometer and the result indicated that the fluorescence of $(CZHQ)_3AI$ can also be quenched by carbon nanotubes (Fig. 6). It can be seen that the emission peak intensities of $(CZHQ)_3AI$ were decreased with gradual increase in concentration of CNTs in DMSO. Meantime, the emission peaks had no obvious change. The phenomenon indicated that the intense interaction of $(CZHQ)_3AI$ and CNTs in excited state happened [22]. Further research toward a better understanding of this action is currently in progress.

4. Conclusions

A novel metal complex (CZHQ)₃Al containing 8hydroxyquinoline aluminum electron transport groups, and carbazole hole-transport groups was designed and synthesized. The optical research showed the absorption had two absorptions peaks (343 nm, 330 nm) and the emission was located at 522 nm in DMSO. The luminescence quantum yield was 0.62 in DMSO. The light emitting can be quenched by electron acceptor and the quenched processes followed the Stern–Volmer equation. The molecular interactions of (CZHQ)₃Al with fullerene (C_{60}) and carbon nanotubes both happened in the excited state. It can be anticipated that the metal complex will have a potential application as an emitting red-light material.

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