

研究简报

## 含有电子传输基团的双齿配体及铕配合物 $\text{Eu}(\text{DBM})_3(\text{DPOP})$ 的制备与发光性能的研究

应 俊 李 斌\* 朱东霞 田爱香

(东北师范大学化学学院多酸科学教育部重点实验室, 长春 130024)

关键词: 铕(III)配合物; 噁二唑功能化配体; 光致发光

中图分类号: O614.33

文献标识码: A

文章编号: 1001-4861(2009)08-1474-04

### Preparation and Photoluminescence Properties of Bidentate Ligand Containing Electro-transporting Group and Its Europium(III) Complex $\text{Eu}(\text{DBM})_3(\text{DPOP})$

YING Jun LI Bin\* ZHU Dong-Xia TIAN Ai-Xiang

(The Key Laboratory of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry,  
Northeast Normal University, Changchun 130024)

**Abstract:** 1, 3, 4-oxadiazole-containing ligand DPOP(DPOP=2-(11-dipyrido[3, 2-a: 2', 3'-c]phenazine)-5-*p*-tolyl-1, 3, 4-oxadiazole) was synthesized by a convenient method and characterized by elemental analysis, IR,  $^1\text{H}$  NMR. Then, corresponding Eu(III) complex  $[\text{Eu}(\text{DBM})_3(\text{DPOP})]$  (DBM=1, 3-diphenyl-1, 3-propanedionate) was prepared and characterized by elemental analysis, IR. The photophysical properties of ligand and its europium complex were investigated. The ligand emitted at 443 nm. There were different PL spectra in solid state and in solution of  $\text{Eu}(\text{DBM})_3(\text{DPOP})$ . There are two fluorescent peaks at 614 nm, 400 nm in dichloromethane solution of  $\text{Eu}(\text{DBM})_3(\text{DPOP})$ , but in solid state only red emission was observed. This result indicated that efficient energy transfer could take place from DPOP ligand to europium ion in Eu-complex solid.

**Key words:** europium(III) complex; oxadiazole-functionalized ligand; photoluminescence

Organic Light-Emitting Diodes(OLEDs) using small organic molecules have been intensively studied after the initial work by Tang and co-workers<sup>[1]</sup> owing to their potential application in the next generation of full-color flat panel display. Highly efficient electroluminescent(EL) materials based on heavy metal coordinated complexes have received tremendous attentions<sup>[2]</sup>. Comparing with porphyrin platinum and cyclometalated complexes, rare-earth complexes are expected to

show high luminance efficiency along with a narrow emission spectra corresponding to  $^5D_x-^7F_x$  transitions, which are well-suited for actual display applications<sup>[3,4]</sup>. However, of the europium complexes, compared with its excellent photoluminescence(PL) properties, a corresponding high performance read device has not yet been available. In previous reports, methods to improve the europium complexes EL performances focused on molecular design and changing of the device structure<sup>[5]</sup>.

收稿日期: 2009-04-20。收修改稿日期: 2009-06-11。

国家自然科学基金(No.50872130)资助项目。

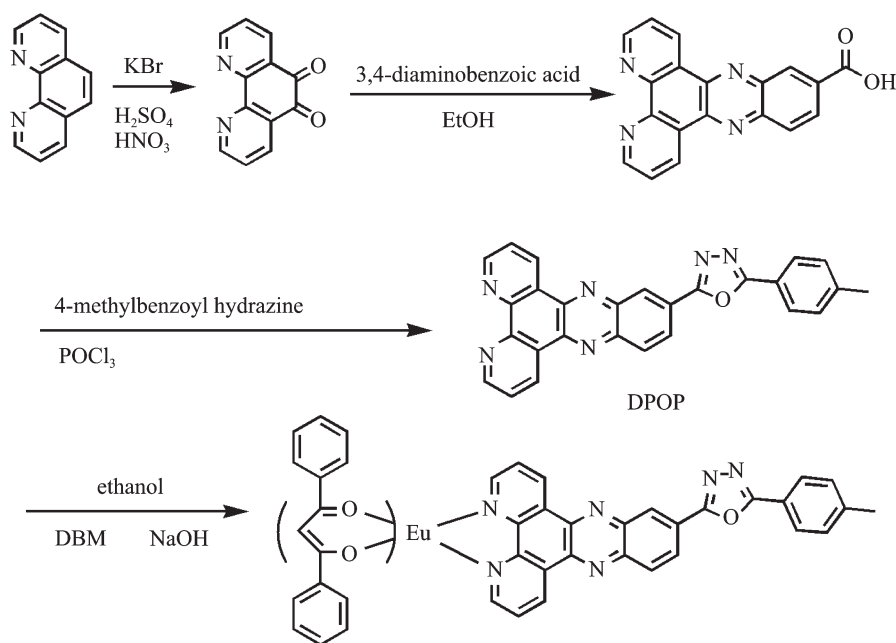
\*通讯联系人。E-mail: lib020@yahoo.cn

第一作者: 应 俊, 男, 29 岁, 硕士研究生; 研究方向: 金属配合物发光材料。

Liang et al.<sup>[6]</sup> designed a new second ligand containing an oxadiazole group by a flexible spacer, and prepared corresponding europium complex-based EL device, their results demonstrate that incorporation of an oxadiazole group not only enhances the charge carrier transport, and thus improving the OLEDs performance, but also simplifies the device structure. Zhang et al.<sup>[7]</sup> designed a new  $\text{Eu}(\text{III})$  complex containing  $\beta$ -diketone ligand with fluorine substituents and corresponding europium complex-based EL device showed promising performances. Wang and co-workers<sup>[8]</sup> designed a second ligand incorporating light-emitting center, hole transporting triphenylamine and electron-transporting phenanthroline fragments, prepared the corresponding  $\text{Eu}(\text{III})$  complex and examined its EL device, and remarkable EL performances were obtained. Cheng et al. reported a series of substituted phenanthrolines and

their europium complexes<sup>[9]</sup>. One of them,  $\text{Eu}(\text{TTA})_3\text{DPPZ}$  ( $\text{TTA}$ =2-thenoyltrifluoroacetate,  $\text{DPPZ}$ =dipyrido [3, 2-a: 2', 3'-c]phenazine), presented excellent EL performance, these results indicate that the design of ligands is crucial to enhance the performance of EL devices based on rare-earth metal complexes<sup>[10]</sup>.

Here we report the synthesis of a bidentate ligand and its  $\text{Eu}(\text{III})$  ternary complex by incorporating light-emitting center, electron-transporting oxadiazole and  $\text{DPPZ}$  fragments into one molecule. The synthetic scheme for ligand 2-(11-dipyrido [3, 2-a: 2', 3'-c] phenazine)-5-*p*-tolyl-1, 3, 4-oxadiazole and corresponding  $\text{Eu}(\text{III})$  complex is summarized in Scheme 1. The purity and composition of the ligand and  $\text{Eu}(\text{III})$  complex were confirmed by  $^1\text{H}$  NMR, IR spectroscopy and elemental analyses.



Scheme 1 Schematic synthesis of DPOP and Eu complex

## 1 Experimental

All materials for synthesis were of analytical grade and used without further purification unless otherwise specified. 1, 10-phenanthroline-5, 6-dione<sup>[11]</sup>,  $\text{Dppz-COOH}$ <sup>[12]</sup>, and 4-methylbenzoic hydrazide were prepared according to literature procedures<sup>[13]</sup> with modification and higher yield.

**Synthesis of DPOP:**  $\text{Dppz-COOH}$  3.27 g (10.0 mmol) and the 4-methylbenzoyl hydrazine 1.50 g (10.0 mmol) were dissolved in 30.0 mL of newly distilled  $\text{POCl}_3$ . The mixture was heated under reflux for 24 h. After excess  $\text{POCl}_3$  was removed by distillation under reduced pressure, the mixture was cooled to room temperature and then poured into ice-water mixture. Precipitate was collected by filtration and washed with sodium hydroxide

solution and water until neutral pH value. The crude product was washed by Soxhlet extraction in dichloromethane(220 mL) for 6 h. The dichloromethane was removed on the rotary evaporator giving a yellow powder. Yield: 40%. IR(KBr disc, 25 °C):  $\nu$ =1616(m), 1 575(s, C=N), 1 488 (s), 1 401(s, aromatic ring) 1 356 (m), 1 312(m), 1 209(w), 1 068(m), 1 031(s, C-O), 921(s), 809(m), 736(s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR(500 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$ =9.40 (m, 2H), 9.22 (m, 2H), 8.76 (m, 1H), 8.50(dd, 1H,  $J$ =2.1, 9Hz), 8.27(dd, 1H,  $J$ =0.6, 9 Hz), 7.72(m, 2H), 7.96(m, 2H), 7.28(m, 2H), 2.41(s, 3H). ppm. Anal. Calc.  $\text{C}_{27}\text{H}_{16}\text{N}_6\text{O}$ : C, 73.63; H, 3.66; N, 3.63%. Found: C, 73.52; H, 3.72; N, 3.56%.

Synthesis of Eu(III) complex: Dibenzoyl methane (HDBM) (0.45 g, 0.6 mmol) and DPOP (0.088 g, 0.2 mmol) were dissolved in hot ethanol(15 mL, 60 °C). A solution of NaOH( $1 \text{ mol} \cdot \text{L}^{-1}$ , 0.6 mL) was added to neutralize the HDBM ligand. Then,  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.073 g, 0.2 mmol) was dissolved in ethanol(2 mL) and added dropwise to the above solution. The solution was stirred at 60 °C for 5 h. Then, the solvent was removed under reduced pressure, and the obtained solid was washed with water several times. After drying, the solid was dissolved in chloroform(5 mL) and vapor diffusion of hexane into the resulting solution gave yellow solid of the complex  $\text{Eu}(\text{DBM})_3\text{DPOP}$ . Yield: 40%. IR(KBr disc, 25 °C): 3 058, 3 025, 2 966, 2 928, 1 549, 1 518, 1 458 (C=O, chelated to  $\text{Eu}^{3+}$ ), 618, 508, 413(O-Eu-O), 1 031 (C-O), 1 575 (C=N), 1 401 (aromatic ring). Anal. Calc.  $\text{C}_{72}\text{H}_{49}\text{EuN}_6\text{O}_7$ : C, 68.52; H, 3.91; N, 6.66%. Found: C, 68.42; H, 3.82; N, 6.56%

## 2 Results and discussion

The UV-Visible spectra of europium complex  $\text{Eu}(\text{DBM})_3(\text{DPOP})$  and ligand DPOP in dichloromethane solution are in Fig.1. The UV-Vis spectrum of DPOP shows four bands at 241, 295, 379, and 401 nm. The former two bands attribute to  $\pi$ - $\pi^*$  transitions, the last two bands are due to  $n$ - $\pi^*$  transitions<sup>[14]</sup>. The UV spectrum of  $\text{Eu}(\text{DBM})_3(\text{DPOP})$  exhibits two ligand (DBM)-centered  $\pi$ - $\pi^*$  transitions at 251, 350 nm which are dominant in the spectrum so that the characteristic absorption of ligand DPOP is obscured. The PL spectra of

$\text{Eu}(\text{DBM})_3(\text{DPOP})$  in solid state and  $\text{CH}_2\text{Cl}_2$  solution excited at 380 nm are shown in Fig.2 and Fig.3. It is very interesting that PL spectrum in dichloromethane solution is different from that in solid state of  $\text{Eu}(\text{DBM})_3(\text{DPOP})$ . There are two fluorescent peaks at 614 nm, 400 nm in dichloromethane solution of  $\text{Eu}(\text{DBM})_3(\text{DPOP})$ , but five sharp emission peaks are shown centered at 580, 592, 613, 652 and 703 nm, assigned to  $^5\text{D}_0 \rightarrow ^7\text{F}_0$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_1$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_3$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  transitions. In Fig.4, the ligand PL spectrum is recorded in dichloromethane

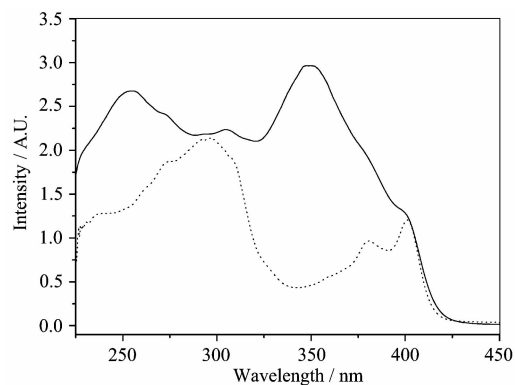


Fig.1 UV-Vis spectra of Eu-complex(solid line) and ligand DPOP(dashed line)

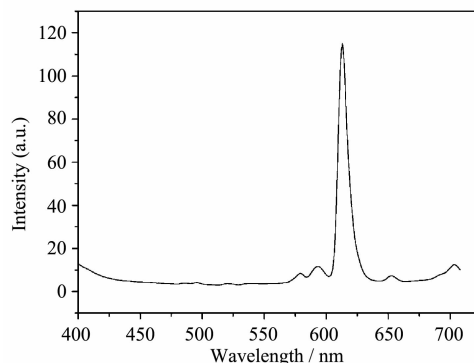


Fig.2 PL spectrum of  $\text{Eu}(\text{DBM})_3(\text{DPOP})$  in solid state

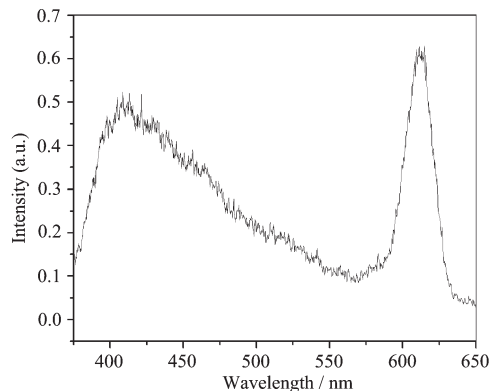


Fig.3 PL spectrum of  $\text{Eu}(\text{DBM})_3(\text{DPOP})$  in  $\text{CH}_2\text{Cl}_2$

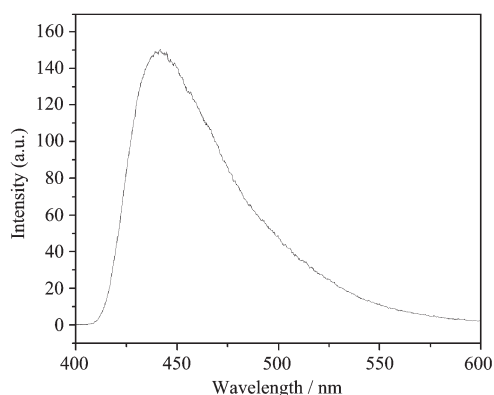


Fig.4 PL spectrum of DPOP

solution emitted at 463 nm. It is not clear why there are different PL spectra in two states of this Eu-complex, but this result indicates that efficient energy transfer could take place from DPOP ligand to europium ion in Eu-complex solid. Among the five peaks, the band at 613 nm from the  $^5D_0 \rightarrow ^7F_2$  electronic dipole transition is the most intensive, indicating low symmetry around the  $\text{Eu}^{3+}$  ion<sup>[15]</sup>.

In conclusion, an oxadiazole containing Eu(III)-dibenzoyl-methanate mixed ligand complex was designed and synthesized. It exhibits bright red light at 613 nm in solid. The work on electroluminescent devices based on the Eu(III) complex using vacuum deposited technique is in progress.

**Acknowledgments:** The authors gratefully thank the financial support from the National Natural Science Foundations of China(No.50872130).

## References:

- [1] Tang C W, Vanslyke S A. *Appl. Phys. Lett.*, **1987**,**51**:913~915
- [2] Baldo M A, O'Brien D F, You Y, et al. *Nature*, **1998**,**395**:151~154
- [3] GUO Jun-Fang(郭俊芳), ZHANG Hong-Jie(张洪杰), FU Lian-She(符连社), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2004**,**20**(5):543~546
- [4] CHENG Yi-Xiang(成义祥), WANG Yun-Chu(王昀初), TAO Zhong-Dong(陶中东), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2000**,**16**(3):523~526
- [5] Kido J, Okamoto Y. *Chem. Rev.*, **2002**,**102**:2357~2368
- [6] Liang F S, Zhou Q G, Cheng Y X, et al. *Chem. Mater.*, **2003**, **15**:1935~1937
- [7] Yu J B, Zhou L, Zhang H J, et al. *Inorg. Chem.*, **2005**,**44**:1611~1618
- [8] Sun M, Xin H, Wang K Z, et al. *Chem. Commun.*, **2003**,**6**: 702~703
- [9] Sun P P, Duan J P, Lih J J, et al. *Adv. Funt. Mater.*, **2003**,**13**: 683~691
- [10] Sun P P, Duan J P, Shih H T, et al. *Appl. Phys. Lett.*, **2000**, **81**:792~794
- [11] Zou X H, Ye B H, Li H, et al. *J. Chem. Soc., Dalton Trans.*, **1999**,**9**:1423~1428
- [12] Ossipov D, Zamaratski E, Chattopadhyaya J. *Helv. Chim. Acta*, **1999**,**82**:2186~2200
- [13] Wang Y P, Xie W F, Li B, et al. *Chin. Chem. Lett.*, **2007**,**18**: 1501~1504
- [14] Bian Z Q, Gao D Q, Wang K Z, et al. *Thin Solid Films*, **2004**, **460**:237~241
- [15] Bian Z Q, Wang K Z, Jin L P. *Polyhedron*, **2002**,**21**:313~319