

Photophysical studies on ternary mixed ligand europium complexes containing pyridyltriazolylmethane and 1,3-diketonate ligands



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ABSTRACT

1,1-Bis[5-(pyridine-2-yl)-1,2,4-triazol-3-yl]methane have been used to prepare ternary lanthanide complexes in which the remaining ligands are different diketonate-anions. The complexes were characterized by various measurements including single-crystal X-ray crystallography. The characteristic photophysical properties of these complexes, i.e. the absorption and luminescence spectra, the metal-centred lifetimes and the overall luminescence yields were measured. All title complexes show strong sharp red emissions in the solid state, corresponding to $^5D_0 \rightarrow ^7F_1$ ($J = 0-3$) transitions with $^5D_0 \rightarrow ^7F_2$ (612–621 nm) as the most prominent one. Three-layer light-emitting diodes based on PVK doped with the title complexes as active layer were fabricated and examined.

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1. Introduction

Europium complexes attracted considerable attention as red light emitting materials, based on the strong metal-centred luminescence of Eu(III) [1–3]. This made Eu(III) complexes to one of the promising candidates for full colour displays which require pure red, green and blue emissions. The literature contains many references concerning the design of devices based on europium complexes with brightness up to 1000 cd m^{-2} [4–6]. Unfortunately significantly high efficiency of these electroluminescent devices has not been achieved so far. One of the important reasons for this is the poor carrier transporting properties (especially electrons) of these complexes. A promising approach for improving these carrier-transporting properties of europium complexes is the insertion of new β -diketones and/or neutral secondary ligands, incorporating electron-transporting and hole-transporting groups into Eu(III) complex molecules [4,7–9]. It is known that 1,3,4-oxadiazole and 1,2,4-triazole derivatives are the most widely used electron-transporting and hole-blocking materials [10]. Several scientific groups focused therefore on the design and synthesis of oxadiazole-functionalized β -diketonate ligands and on the corresponding lanthanide complexes. The literature contains several interesting results which show the effectiveness of this strategy to improve carrier transporting proper-

ties of Eu(III) complexes [8–9]. It should be noted, however, that the use of triazole derivatives for this purpose has not been found in the literature. Recently we have shown that Eu(III) complexes with pyridyltriazoles as secondary ligands lead to good photoluminescent properties both in solutions and solid state [11,12]. In the present paper we describe the structures and photophysical properties of new ternary complexes of ions europium(III) with mixed-ligand donor sets consisting of diketonate-anions and 1,1-bis[5-(pyridine-2-yl)-1,2,4-triazol-3-yl]methane (Fig. 1) to further elaborate the above mentioned strategy.

2. Experimental

2.1. Materials and methods

All reagents and solvents employed were commercially available and used as received without further purification. H_2L was prepared according to literature [13]. Elemental analyses of C, H and N were performed with a Perkin–Elmer 240 C analyzer. IR spectra were measured with a Nicolet Nexus 470 FTIR spectrometer with KBr pellets in the range $4000\text{--}400 \text{ cm}^{-1}$. Thermal stability (TG-DTA) studies were carried out with a Paulik–Paulik–Erdey Q-derivatograph. Absorption spectra were recorded on a Perkin–Elmer Lambda-9 UV/Vis/NIR spectrophotometer. Solid-state excitation and fluorescence spectra were recorded on a Horiba Jobin–Yvon Fluorolog FL-3-22 spectrofluorometer equipped with a 450 W Xe lamp. Quantum yields were determined under ligand excitation on the same

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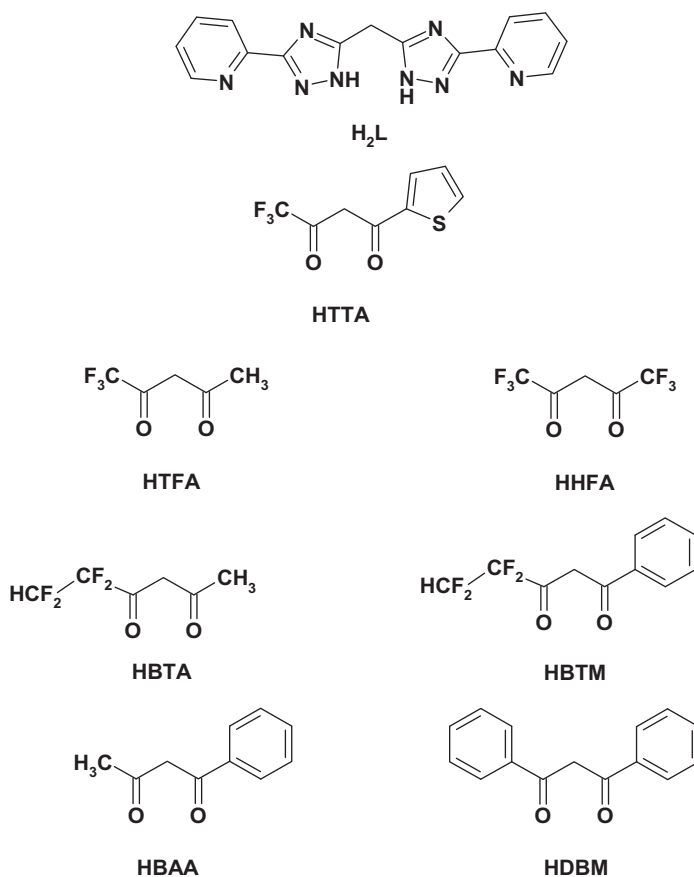


Fig. 1. Molecular structures and abbreviations of the used ligands.

instrument by an absolute method using a home-modified integrating sphere. Lifetime measurements were performed on a Horiba Fluorocube lifetime instrument by a time-correlated single-photon counting method using a 365 nm LED excitation source. The current-density–luminance–voltage characteristics of the OLEDs were measured by Keithley source measurement unit with a calibrated silicon photodiode. Electroluminescence spectra were taken by a multichannel S2000 Ocean Optics spectrometer. All measurements were carried out in ambient atmosphere at room temperature.

Three-layer type OLED devices with the structure (**1**) ITO/NPB(40 nm)/PVK:Eu(DBM)₂HL (60 nm)/AlQ₃(30 nm)/LiF (2 nm)/Al (100 nm); (**2**) ITO/NPB(40 nm)/PVK:Eu(TTA)₂HL (60 nm)/AlQ₃(30 nm)/LiF (2 nm)/Al (100 nm) were fabricated on glass substrates with 100 nm thickness. *N,N'*-Diphenyl-*N,N'*-bis(1-naphthyl)(1,1'-biphenyl)-4,4'-diamine – NPB was used as hole-transporting material. Thin films of [Eu(DBM)₂(HL)] and [Eu(TTA)₂(HL)] dissolved in a PVK solution at 5% w/w were obtained by spin coating glass surfaces using doping in chlorobenzene. Remaining organic layers were sequentially deposited at a rate in the range of 0.1–0.3 nm/s onto the substrates by high-vacuum (10⁻⁵ mbar) thermal evaporation techniques.

2.2. Synthesis

The title complexes were obtained by general procedures as follows.

Eu(NO₃)₃·6H₂O (446 mg, 1 mmol) (Gd(NO₃)₃·6H₂O for **8**) were dissolved in 10 ml of MeOH. Then, a solution of 332 mg (1 mmol) of triazole's ligand H₂L in 5 ml of MeOH/water (1:1 v/v) were added dropwise into reactant solutions. After then 2.2 mmol of re-

lated diketone in 5 ml MeOH and 120 mg of NaOH were added and mixture was allowed to settle at 60 °C and then stirred for 1 h. After being allowed to cool, the precipitate was washed with cold MeOH. Crude solid was recrystallized from small amount of methanol to give a yellowish powder.

Gadolinium complexes was prepared by same procedure/

[Eu(DBM)₂(HL)] (**1**) Yield: (82%). *Anal. Calc.* for C₄₅H₃₃EuO₄N₈: C, 59.87; H, 3.77; N, 12.42. Found: C, 59.94; H, 3.62; N, 12.31%. IR (KBr, cm⁻¹): ν 3058 (m), 1596 (s), 1550 (s), 1518 (s), 1478 (s), 1456 (s), 1402 (s), 1310 (m), 1222 (m), 1068 (m), 724 (m), 614 (m), 514 (w).

[Eu(TFA)₂(HL)·MeOH]·MeOH (**2**) Yield: (51%). *Anal. Calc.* for C₂₇H₃₁EuF₆O₆N₈: C, 39.10; H, 3.76; N, 13.51. Found: C, 39.24; H, 3.62; N, 13.62%. IR (KBr, cm⁻¹): ν 1653 (s), 1601 (m), 1522 (m), 1498 (s), 1275 (s), 1211 (s), 1149 (s), 785 (m), 654 (m).

[Eu(HFA)₂(HL)] (**3**) Yield: (47%). *Anal. Calc.* for C₂₅H₁₇EuF₁₂O₄N₈: C, 34.39; H, 1.96; N, 12.83. Found: C, 34.52; H, 1.87; N, 12.74%. IR (KBr, cm⁻¹): ν 1664 (s), 1608 (m), 1530 (m), 1490 (s), 1256 (s), 1206 (s), 1144 (s), 796 (m), 662 (m).

[Eu(TTA)₂(HL)] (**4**) Yield: (79%). *Anal. Calc.* for C₃₁H₂₃EuF₆O₄N₈·S₂: C, 41.30; H, 2.56; N, 12.43. Found: C, 41.26; H, 2.33; N, 12.56%. IR (KBr, cm⁻¹): ν 3416 (m), 1623 (s), 1605 (s), 1538 (s), 1505 (s), 1413 (s), 1353 (s), 1306 (s), 1183 (s), 1149 (s), 786 (m), 717 (m), 642 (m), 518 (m).

[Eu(BAA)₂(HL)] (**5**) Yield: (83%). *Anal. Calc.* for C₃₅H₃₁EuO₄N₈: C, 53.92; H, 4.00; N, 14.37. Found: C, 53.69; H, 3.78; N, 14.52%. IR (KBr, cm⁻¹): ν 3412 (m), 1596 (s), 1568 (s), 1516 (s), 1484 (s), 1452 (s), 1394 (s), 1284 (m), 724 (m).

[Eu(BTA)₂(HL)·MeOH] (**6**) Yield: (57%). *Anal. Calc.* for C₂₈H₂₉EuF₈O₅N₈: C, 39.04; H, 3.39; N, 13.00. Found: C, 38.91; H, 3.47;

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