

Photoluminescence Studies on Dy(III)-Dibenzoylmethane Ternary Complexes with 1,10-Phenanthroline Derivatives

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Abstract: Lanthanide β -diketonate complexes have been intensively studied as emitting materials in organic light emitting diodes (OLEDs). In this study, the binary complex of Dy(III) with dibenzoylmethane (DBM) was synthesized. Four ternary complexes of Dy(III) were obtained by the addition of 1,10-phenanthroline (phen) and its derivatives as second ligand adduct. The isolated complexes were characterized by elemental analysis, infrared (IR) spectra, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and fluorescence spectrometry. All complexes are shown to be fluorescing. A strong emission band at blue-green region was observed from all complexes at 461 nm, 484 nm and 526 nm excited at 333 nm. Tris-(dibenzoylmethane)(4,7-dimethyl-1,10-phenanthroline)dysprosium(III) [Dy(DBM)₃dmphen] offered the highest luminescent intensity compared to the others and tris-(dibenzoylmethane)(4,7-diphenyl-1,10-phenanthroline)dysprosium(III) [Dy(DBM)₃dpphen] found to be the most thermally stable.

Key words: Binary complexes · Ternary complexes · Lanthanide β -diketonates complexes · Photoluminescence · OLEDs

INTRODUCTION

Luminescent organic and organometallic compounds have attracted much attention because of their great potential for the application as organic light emitting diodes (OLEDs) materials due to their high stability and efficiency [1-3]. Rare earth (RE) metal complexes have always been the most popular central metal ion for making electroluminescent devices owing to their inherent sharp emission bands and potentially high internal quantum efficiency is very promising candidate for next generation of flat panel display with low-voltage drive [4-7]. The high intensity of luminescence resulting from 4f-4f transitions of RE³⁺ after the harvesting of both singlet and triplet excitons produced on the surrounding ligands is also another added advantages of the RE complexes as OLEDs [8-10]. The complexes of β -diketonates (1,3-diketones) with rare earth ions are the most popular and the most investigated rare earth coordination compounds as β -diketonates ligand act as 'antenna' in term of organic chromophore to sensitize the lanthanide ion [11-13]. However, the progress in the application of these complexes as organic light emitting diodes materials is

rather slow due to the several practical limitations in manufacturing especially related to the chemical instability of the complex and the inefficiency of the transition. One of the serious problem in getting high intensity luminescence is due to the quenching effect of the functional group of ligands such as hydroxyl group from water molecules easily coordinated as hydrated molecules [14, 15]. The presence of water molecule can be avoided by replacing H₂O molecules with another ligands such as 1,10-phenanthroline (Phen) derivatives as reported by Bian *et al.* [16] to form ternary complexes of Eu(DBM)₃(2,4'-dimethylaminophenyl)imidazo [4,5-f] 1,10-phenanthroline). They found that this ternary complex has improved the volatility, thermal stability and carrier transport ability of the RE³⁺ complexes. Thus, research work on the synthesis of new dysprosium(III) complexes containing new ligands to produce a number of novel luminescent complexes as emitters and electron transporters in OLED research are actively pursued [17-21]. In the present work, the dysprosium(III)-dibenzoylmethane binary and ternary complexes were synthesized. The luminescence properties of these complexes were also presented.

MATERIALS AND METHODS

Chemicals: Dysprosium(III) nitrate hydrate-99.9% and dibenzoylmethane-98% (DBM) were purchased from Aldrich. 1,10-phenanthroline-99+% (phen) was purchased from Acros Organics. Bathophenanthroline-98+% (dpphen), 4,7-dimethyl-1,10-phenanthroline-98+% (dmphen) and 3,4,7,8-tetramethyl-1,10-phenanthroline-98+% (tmphen) were purchased from Alfa Aesar. Pure ethanol from QRec and the other solvents from Merck. All chemicals were used as received.

The Synthesis of Binary Complex (Dy(DBM)₃): The synthesis method was adopted with some modifications according to Junfeng Fang *et al.* [11]: About 3 mmol of dibenzoylmethane was dissolved in 30 ml hot ethanol. Then, 5 ml sodium hydroxide solution (0.6 mmol/ml) was added and the mixture was stirred at 50-60 °C while 10 ml of dysprosium(III) nitrate solution (0.1 mmol/ml) was added dropwise. The reaction mixture was heated and stirred at 50-60 °C for 2 hours and was then cooled to room temperature. The resulting precipitate was filtered off, washed with water and cool ethanol in turn. The schematic synthesis of Dy(DBM)₃ is shown in Fig. 1.

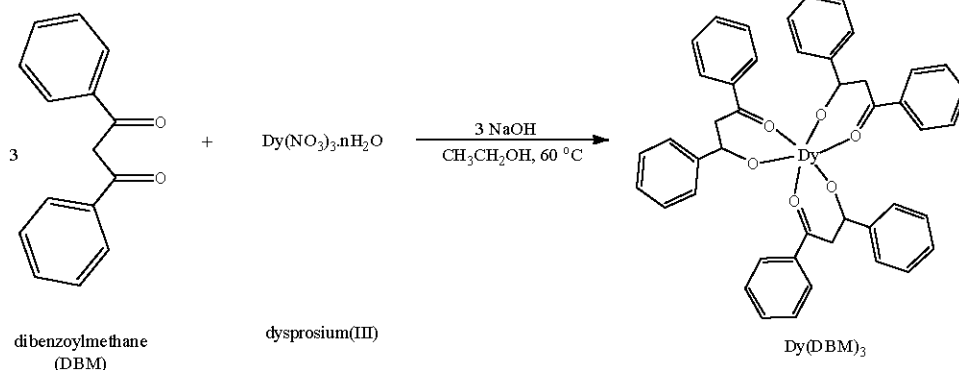


Fig. 1: The schematic synthesis of Dy(DBM)₃.

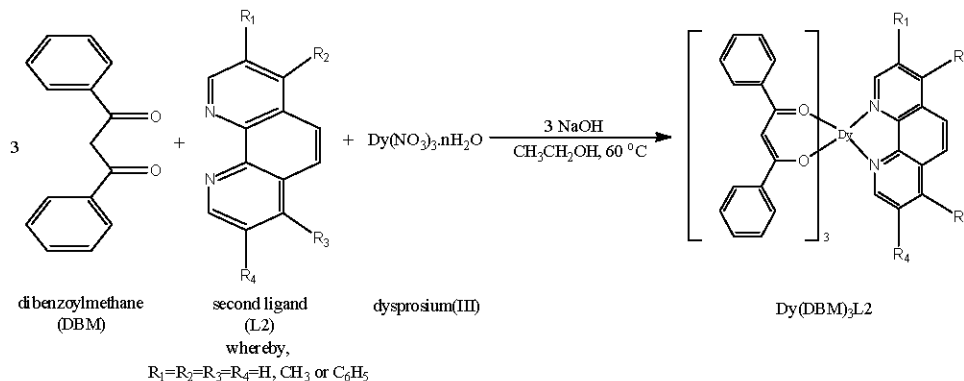


Fig. 2: The schematic synthesis of Dy(DBM)₃L₂.

The Synthesis of Ternary Complexes (Dy(DBM)₃L₂):

About 3 mmol of dibenzoylmethane and 1 mmol of second ligand (phen/dmphen/tmphen/dpphen) were dissolved in 30 ml hot ethanol. Then, 5 ml sodium hydroxide solution (0.6 mmol/ml) was added and the mixture was stirred at 50-60 °C while 10 ml of lanthanide(III) nitrate solution (0.1 mmol/ml) was added dropwise. The reaction mixture was heated and stirred at 50-60 °C for 2 hours and was then cooled to room temperature. The resulting precipitate was filtered off, washed with water and cool ethanol in turn. The schematic synthesis of Dy(DBM)₃L₂ is shown in Fig. 2.

The Spectroscopy Measurements: The elemental analysis of these complexes was carried out with Perkin Elmer 2400 Series II elemental analyzer. The infrared absorption spectra of the free ligands and complexes in KBr pellets were recorded in the spectral range 400-4000 cm⁻¹ on a Perkin Elmer spectrophotometer. The thermal analysis was carried out with Perkin Elmer. The optical properties of these complexes were also studied by observing the fluorescence emission spectra with a Perkin Elmer LS 55. All measurements were performed in ambient atmosphere at room temperature.

Table 1: Elemental analysis data for dysprosium(III) binary and ternary complexes

Compounds	%C		%H		%N	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Dy(DBM) ₃	64.47	64.42	4.69	4.49	0	0.63
Dy(DBM) ₃ phen	67.22	66.89	4.65	4.40	2.75	2.93
Dy(DBM) ₃ dmphen	67.71	68.21	4.91	4.83	2.68	2.98
Dy(DBM) ₃ tmphen	68.18	68.21	5.16	5.27	2.61	2.85
Dy(DBM) ₃ dpphen	70.79	71.14	4.74	4.68	2.39	2.56

Table 2: The IR data (cm⁻¹) of free ligands and complexes with their assignments

Compounds	Main absorption bands and their assignments
DBM	3064 (μ =C-H) 1597 (μ _{as} C=O) 1534 (μ _{as} C-O)
Phen	3384 (μ N-H) 1586 (μ _s C=C) 1421 (μ C=N)
Dmphen	3402 (μ N-H) 1586 (μ _s C=C) 1416 (μ C=N)
Tmphen	3422 (μ N-H) 1566 (μ _s C=C) 1421 (μ C=N)
Dpphen	3422 (μ N-H) 1553 (μ _s C=C) 1411 (μ C=N)
Dy(DBM) ₃	3417 (μ N-H) 3059 (μ =C-H) 1600 (μ _{as} C=O) 1552 (μ _s C=C) 1518 (μ _{as} C-O)
Dy(DBM) ₃ phen	3425 (μ N-H) 3056 (μ =C-H) 1595 (μ _{as} C=O) 1551 (μ _s C=C) 1516 (μ _{as} C-O) 1414 (μ C=N)
Dy(DBM) ₃ dmphen	3427 (μ N-H) 3057 (μ =C-H) 1596 (μ _{as} C=O) 1551 (μ _s C=C) 1516 (μ _{as} C-O) 1416 (μ C=N)
Dy(DBM) ₃ tmphen	3415 (μ N-H) 3056 (μ =C-H) 1597 (μ _{as} C=O) 1551 (μ _s C=C) 1516 (μ _{as} C-O) 1416 (μ C=N)
Dy(DBM) ₃ dpphen	3412 (μ N-H) 3056 (μ =C-H) 1595 (μ _{as} C=O) 1551 (μ _s C=C) 1518 (μ _{as} C-O) 1414 (μ C=N)

RESULTS AND DISCUSSION

Elemental Analysis: The elemental analysis data are in good concordance with the general formula of Dy(DBM)₃ and Dy(DBM)₃L₂ as shown in Table 1.

IR Spectra: The main IR absorption bands and their assignments are summarized in Table 2. The assignments are made by comparison with known related compounds and functional groups. The IR spectra data presented a displacement of the C-O stretching from 1534 cm⁻¹ in the free DBM ligand to 1518 cm⁻¹ for Dy(DBM)₃ and Dy(DBM)₃dpphen and 1516 cm⁻¹ for Dy(DBM)₃phen, Dy(DBM)₃dmphen and Dy(DBM)₃tmphen suggesting that

this ligand is coordinated to the dysprosium(III) ion through the oxygen atom. Besides that, the displacement of the N-H stretching from 3384 cm⁻¹, 3402 cm⁻¹, 3422 cm⁻¹ and 3422 cm⁻¹ in the free phen, dmphen, tmphen and dpphen ligands to 3425 cm⁻¹, 3427 cm⁻¹, 3415 cm⁻¹ and 3412 cm⁻¹ for Dy(DBM)₃phen, Dy(DBM)₃dmphen, Dy(DBM)₃tmphen and Dy(DBM)₃dpphen respectively indicates that second ligand(L₂) is coordinated to the dysprosium(III) ion through the nitrogen atom.

Thermal Analysis: Thermogravimetric and differential thermal analyses (TG-DTA) provide important information on vacuum-deposition behaviors of the complexes. TG-DTA curves (Fig. 3) showed that the binary and

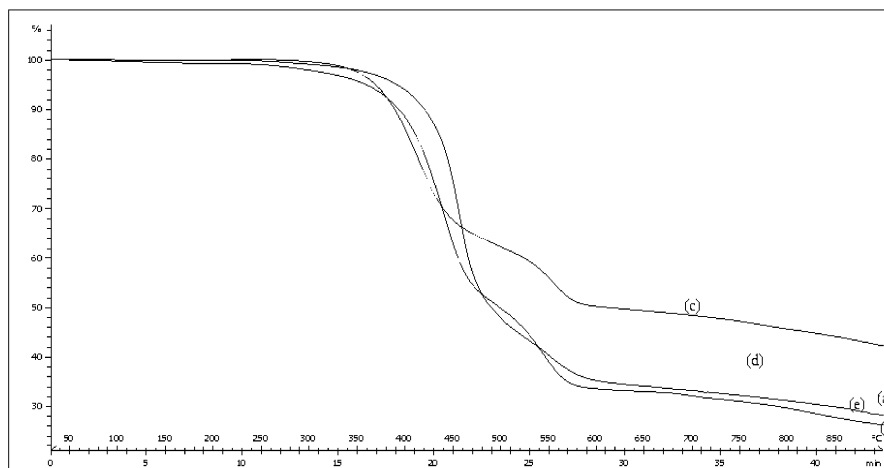


Fig. 3: The TG-DTA curves of (a) Dy(DBM)₃ (b) Dy(DBM)₃phen (c) Dy(DBM)₃dmphen (d) Dy(DBM)₃tmphen (e) Dy(DBM)₃dpphen.

Table 3: Summary of TG-DTA curves of complexes

Compounds	Temperature Range (°C)	Weight Loss (%)	Initial Decomposition Temperature (°C)	Residue(%)
Dy(DBM) ₃	28.80-483.21	36.1064	415	63.8738
	483.21-640.24	26.1178		37.7561
	640.24-903.66	5.7413		32.0147
Dy(DBM) ₃ phen	28.89-503.43	50.4164	438	49.5814
	503.43-637.82	16.6126		32.9685
	637.82-904.66	6.9943		25.9746
Dy(DBM) ₃ dmpphen	29.88-497.75	37.4448	412	62.5568
	497.75-651.69	13.3559		49.2009
	651.69-903.68	7.1896		42.0113
Dy(DBM) ₃ tmphen	30.13-516.83	49.2237	430	50.7898
	516.83-667.32	10.8823		39.9075
	667.32-903.47	6.7252		33.1823
Dy(DBM) ₃ dpphen	28.89-538.77	57.7137	455	42.2678
	538.77-903.69	14.3071		27.9607

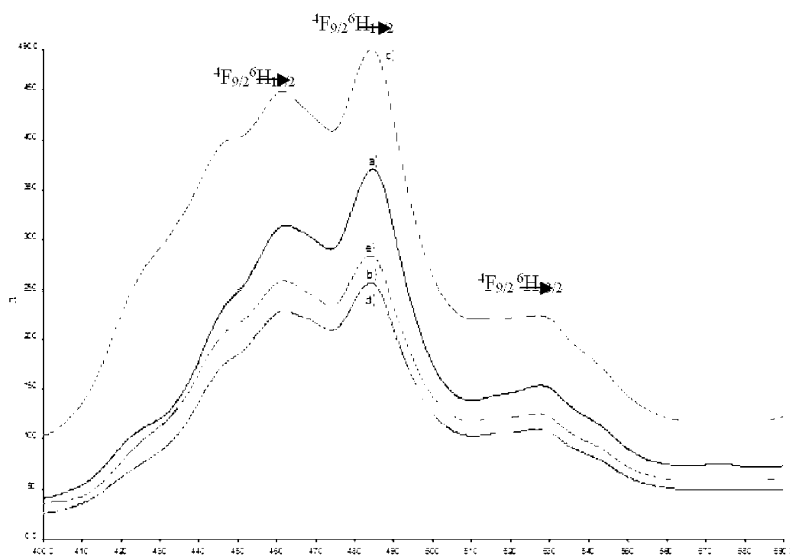


Fig. 4: The emission spectra of (a) Dy(DBM)₃ (b) Dy(DBM)₃phen (c) Dy(DBM)₃dmpphen (d) Dy(DBM)₃tmphen (e) Dy(DBM)₃dpphen

ternary complexes are chemically stable from the room temperature up to 300 °C. Over 300 °C, all the complexes undergo several steps of decomposition. The summary of several decomposition steps of each complex has been shown in Table 3. Based on initial decomposition temperature (IDT) in TG-DTA curves, the complexes presented the following order of thermal stability: Dy(DBM)₃dmpphen < Dy(DBM)₃ < Dy(DBM)₃tmphen < Dy(DBM)₃phen < Dy(DBM)₃dpphen.

Luminescence of Dysprosium (III) Complexes:

Emission spectra of dysprosium (III) complexes were shown in Figure 4. All complexes possess three apparent emission peaks at 461 nm, 484 nm and 526 nm

under the excitation of 333 nm. These indicate the $^4F_{9/2}^6 \rightarrow H_J$ ($J=15/2$ and $13/2$) transitions. All complexes exhibit strong blue emission at 484 nm correspond to the $^4F_{9/2}^6 \rightarrow H_{15/2}$ transition. Dy(DBM)₃dmpphen exhibit the highest luminescent intensity followed by Dy(DBM)₃, Dy(DBM)₃dpphen, Dy(DBM)₃phen, Dy(DBM)₃tmphen respectively. The emission spectra also show a high background from a ligand-based emission band [22]. The presence of ligand-based emission band indicates the luminescence of ligand cannot be quenched by the coordination to Dy(III) ions in their complexes [23]. On the other hand, there is no fluorescence characteristic for dysprosium (III) complexes under UV light at room temperature.

Energy Transfer Between the Ligands and Dysprosium

(III): Generally, the sensitization pathway in luminescence of dysprosium(III) complexes consists of excitation of the ligands into their excited singlet state, subsequent intersystem crossing of the ligands to their triplet state and energy transfer from the triplet state of the ligands to the 4F_7 manifold of Dy(III) ion, following by internal conversion to the emitting $^4F_{9/2}$ state; finally, the Dy(III) ion emits when transition to the ground state occurs [24].

According to the intramolecular energy transfer mechanism, the efficiency depends on two energy transfer process. First, the energy transfer from the lowest triplet energy level of the ligand to the resonant energy level of the Ln(III) ion by Dexter's resonant exchange interaction [25] and secondly, the inverse energy transfer from Ln(III) ion to organic ligand by a thermal deactivation mechanism [21, 26]. The back energy transfer process will take place easily if the energy difference is too small [24, 27].

In order to demonstrate the energy transfer process of dysprosium(III) complexes, the differences between triplet energy level of each ligands and excited state of Dy(III) ion have been calculated. The triplet energy level of DBM (20520 cm^{-1} and dpphen (20900 cm^{-1}) were lower than the $^4F_{9/2}$ level of Dy(III) ion (21100 cm^{-1}). Thus, the energy transfer cannot proceed efficiently as been reported by Wang *et al.* [27] that small energy differences between the ligand, 2,2'-(1,2-naphthalene)bis(oxy)]bis [N-(phenylmethyl)]acetamide and terbium(III) could result in non-radiative deactivation of the terbium(III) emitting state. The triplet energy level of phen (22100 cm^{-1}), dmphen (21551 cm^{-1}) and tmphen (21691 cm^{-1}) were higher than the $^4F_{9/2}$ level of Dy(III) ion (21100 cm^{-1}). The energy gaps, $\Delta E(^3\pi\pi^* \rightarrow ^4F_{9/2})$, for phen, dmphen and tmphen exhibit 1000 cm^{-1} , 451 cm^{-1} and 591 cm^{-1} respectively, the energy transfer process is effective for Dy(DBM)₃phen, Dy(DBM)₃dmphen and Dy(DBM)₃tmphen. However, their energy gaps between triplet state of ligand and excited state of Dy(III) ion, $\Delta E(^3\pi\pi^* \rightarrow ^4F_{9/2})$, are too low, back energy transfer process may also take place, therefore, quench the luminescence of dysprosium(III) complexes [24, 27, 28]. The fluorescence characteristic of the dysprosium(III) complexes under UV light cannot be observed at room temperature because of the quenching of the emission by the back energy transfer process [27].

CONCLUSIONS

Five dysprosium(III) complexes have been successfully synthesized, characterized and their luminescent properties shown to be encouraging. All complexes are shown to be fluorescing at a blue-green

region at 461 nm, 484 nm and 526 nm. The presence of 4,7-dimethyl-1,10-phenanthroline in ternary complexes shows the highest luminescence intensity, on the other hand, decrease the thermal stability. Tris-(dibenzoylmethane) (4,7-diphenyl-1,10-phenanthroline) dysprosium (III) [Dy(DBM)₃dpphen] was found to has the excellent thermal stability. The choice of second ligand is very critical condition in order to compromise the important of fluorescing intensity and also the thermal stability.

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