Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 152 (2016) 304–310

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, photoluminescence and biological properties of terbium(III) complexes with hydroxyketone and nitrogen containing heterocyclic ligands

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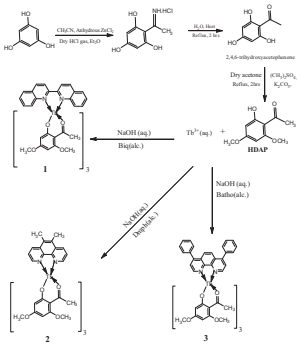
HIGHLIGHTS

- The ligand has been synthesized and these complexes have been prepared first time.
- These complexes emit bright green light which can be significant for display devices.
- The complexes have been investigated for biological activities also.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 August 2014
Received in revised form 18 July 2015
Accepted 22 July 2015
Available online 23 July 2015

Keywords:
Luminescence
Bright green
Tb^{3+}
Antimicrobial activity
Antioxidant

ABSTRACT

The ternary terbium(III) complexes [Tb(HDAP)$_3$·biq], [Tb(HDAP)$_3$·dmph] and [Tb(HDAP)$_3$·bathophen] were prepared by using methoxy substituted hydroxyketone ligand HDAP (2-hydroxy-4,6-dimethoxyace tophenone) and an ancillary ligand 2,2-biquinoline or 5,6-dimethyl-1,10-phenanthroline or bathophenanthroline respectively. The ligand and synthesized complexes were characterised based on elemental analysis, FT-IR and ^{1}H NMR. Thermal behaviour of the synthesized complexes illustrates the general decomposition patterns of the complexes by thermogravimetric analysis. Photophysical properties such as excitation spectra, emission spectra and luminescence decay curves of the complexes were investigated in detail. The main green emitting peak at 548 nm can be attributed to $^5D_4 \rightarrow {}^7F_5$ of Tb^{3+} ion. Thus, these complexes might be used to make a bright green light-emitting diode for display purpose. In addition the in vitro antibacterial activities of HDAP and its Tb(III) complexes against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and antifungal activities against *Candida albicans* and *Aspergillus niger* are reported. The Tb^{3+} complexes were found to be more potent antimicrobial agent as compared to the ligand. Among all these complexes, [Tb(HDAP)$_3$·bathophen] exhibited excellent antimicrobial activity which proves its potential usefulness as an antimicrobial agent. Furthermore, in vitro antioxidant activity tests were carried out by using DPPH method which indicates that the complexes have considerable antioxidant activity when compared with the standard ascorbic acid.

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http://dx.doi.org/10.1016/j.saa.2015.07.082
1386-1425/

1. Introduction

In recent 20 years, the interest of the scientific community regarding optical properties of organolanthanide complexes has been increased because of their intriguing applications in electronic technological field especially in flat panel displays and organic light emitting diodes (OLEDs) [1–3]. The emission in these complexes originates from electronic transitions within the inner f-orbital of the central ion [4,5]. These lanthanide complexes exhibit unique photoluminescent properties such as large stokes shifts, high luminescence efficiencies, long fluorescence decay time and extremely sharp emission spectra [6]. On account of their excellent photoluminescent properties these complexes have also been utilised in luminescent solar concentration [7], optical fibres for data transmission [8], pH sensing [9] and UV dosimeters [10]. Moreover, it is worth to mention that some of these complexes find extensive use in medical diagnosis for instance as magnetic resonance imaging (MRI) contrast agents [11].

Among the lanthanide ions, trivalent Eu^{3+} and Tb^{3+} ions have attracted more attention due to their high luminescence intensity as well as high colour purity [12–14]. The organolanthanide complexes have very bright luminescence and their intensity depends upon radiative and non-radiative process with in a complex [15–17] and energy transfer from organic ligand to central metal ion by "antenna effect", which can increase the luminescence efficiency [5,18–21]. The β-hydroxyketone ligand is one of the major antenna ligand which is found to sensitise Tb^{3+} ion luminescence magnificently. The luminescence is further enhanced by the introduction of ancillary ligand in Tb(III) complexes. The literature study reveals that many lanthanide complexes also exhibited interesting antimicrobial and antioxidant activities [22,23]. Therefore, with an aim to develop new photoluminescent materials and potent antimicrobial and antioxidant agents, we successfully synthesized Tb(III) complexes by incorporating nitrogen containing heterocyclic ancillary ligand.

In present work, a β-hydroxyketone ligand 2-hydroxy-4,6-dimethoxyacetophenone (HDAP) was synthesized. With this β-hydroxyketone as the first ligand and 2,2-biquinoline (biq) or 5,6-dimethyl-1,10-phenanthroline (dmph) or bathophenanthroline (bathophen) as an ancillary ligand, three new terbium(III)complexes [$Tb(HDAP)_3$·biq], [$Tb(HDAP)_3$·dmph] and [$Tb(HDAP)_3$·bathophen] were synthesized. The compositions of these complexes were ascertained by elemental analysis, IR, ^1H NMR spectra and thermal behaviour was perceived by TG–DTA curves. The photoluminescent properties were investigated by excitation spectra, emission spectra and luminescence decay curves. The photoluminescent (PL) studies demonstrate that Tb(III) complexes exhibit bright green colour in solid state at room temperature. The excellent bright green luminescence of these Tb(III) complexes suggest their potential application in display devices. We have also explicated in vitro antimicrobial activities and antioxidant activities of ligand and its corresponding Tb(III) complexes employing tube dilution method and DPPH method respectively in detail.

2. Experimental

2.1. Materials and methods

2,2-Biquinoline, 5,6-dimethyl-1,10-phenanthroline, bathophenanthroline and terbium nitrate pentahydrate were purchased from Sigma–Aldrich. Other reagents were of analytical grade, and used without any further purification.

The elemental analysis (C, H, N) for the synthesized ligand HDAP and the Tb^{3+} complexes were carried out using thermo scientific flash 2000 elemental analyzer, ^1H NMR spectra were recorded on Bruker Avance II 400 spectrometer (400 MHz) using dimethylsulfoxide (DMSO) as solvent, IR spectra (4000–400 cm^{-1}) were recorded at resolution 4 cm^{-1} on Perkin Elmer spectrum 400 FT-IR spectrometer with KBr pellets. Thermogravimetric analysis was carried on a SDT Q600 V20.9 Build 20 thermal analyzer from 20 to 1200 °C at heating rate of 10 °C/min under nitrogen atmosphere. Photoluminescence excitation (PLE), emission (PL) spectra and fluorescence lifetime decay were conducted by using Hitachi F-7000 fluorescence spectrophotometer equipped with Xe-lamp at room temperature in solid state. Antimicrobial and antioxidant activities were determined by tube dilution method and DPPH method respectively.

2.2. Synthesis

The synthetic routes of ligand HDAP and complexes **1–3** are shown in Scheme 1, which were synthesized from the reaction of the ligand HDAP, ancillary ligand and $Tb(NO_3)_3·5H_2O$ in ethanol solution.

2.2.1. Synthesis of ligand (HDAP)

The hydroxyketone ligand (HDAP) was synthesized by following Houben–Hoesch reaction mechanism between phloroglucinol and acetonitrile according to the method cited in literature [24]. White powder with 85% yield was obtained. The elemental analysis data of HDAP ($C_{10}H_{12}O_4$) is found (calculated)% C, 61.14 (61.22); H, 6.18 (6.16); O, 32.48 (32.62). IR (KBr) cm^{-1} 3430 (b), 3009 (w), 2943 (w), 2847 (w), 1630 (s), 1457 (m), 1422 (m), 1366 (s), 1324 (m), 1270 (s), 1221 (s), 1207 (s), 1154 (s), 1112 (m), 1079 (m), 1045 (w), 896 (m), 835 (m), 658 (m), 606 (w). ^1H NMR (400 MHz, DMSO): δ 2.52 (s, 3H, CH_3), 3.83 (s, 6H, OCH_3), 6.02 (s, 2H, Ar–H), 13.84 (s, 1H, OH).

2.2.2. Synthesis of complex $Tb(HDAP)_3$·biq (**1**)

The complex $Tb(HDAP)_3$·biq was prepared by mixing ethanolic solutions of HDAP (0.58 g, 3 mmol) and biq (1 mmol) with an aqueous solution of $Tb(NO_3)_3·5H_2O$ (1 mmol) with constant stirring on magnetic stirrer. The pH of mixture was adjusted to 7–8 with 0.05 M NaOH solution. This resulted into formation of white precipitates. These precipitates were stirred for 3 h at 35 °C and then allowed to stand for 1 h. The precipitates were filtered, washed with water, ethanol, dried in air and then in vacuum desiccators to obtain complex $Tb(HDAP)_3$·biq (**1**). White powder with 86% yield was obtained. The elemental analysis data of $Tb(HDAP)_3$·biq ($C_{48}H_{45}O_{12}N_2Tb$) is found (calculated)% C, 57.56 (57.60); H, 4.54 (4.50); N, 2.78 (2.80). IR (KBr):cm^{-1} 3008 (m), 2947 (m), 1616 (s), 1593 (s), 1534 (s), 1516 (s), 1496 (s), 1418 (m), 1384 (s), 1328 (m),1263 (m), 1220 (s), 1212 (m), 1159 (m), 1128 (s), 1057 (m), 1013 (w), 936 (m), 869 (m), 839 (m), 829 (s), 787 (m), 738 (s), 625 (m), 538 (w), 471 (w). ^1H NMR (400 MHz, DMSO): δ 2.67 (bs, 9H, CH_3), 3.52 (bs, 18H, OCH_3), 6.31 (bs, 6H, Ar–H), 7.63 (d, 2H, biq), 7.84 (d, 2H, biq), 8.02 (d, 2H, biq), 8.21 (d, 2H, biq), 8.49 (d, 2H, biq), 8.83 (d, 2H, biq).

2.2.3. Synthesis of complex $Tb(HDAP)_3$·dmph (**2**)

Same procedure as for $Tb(HDAP)_3$·biq (**1**) but the mixture with HDAP (3 mmol) and dmph (1 mmol) and 1 mmol $Tb(NO_3)_3·5H_2O$. The complexes $Tb(HDAP)_3$·dmph (**2**) was obtained as a white powder with 85% yield. The elemental analysis data of $Tb(HDAP)_3$·dmph ($C_{44}H_{45}O_{12}N_2Tb$) is found (calculated)% C, 55.42 (55.46); H, 4.70 (4.72); N, 2.93 (2.94).

IR (KBr):cm^{-1} 3006 (m), 2965 (m), 2939 (m), 1615 (s), 1573 (s), 1533 (s), 1495 (s) 1450 (m), 1417 (m), 1364 (s), 1329 (m), 1262 (s), 1220 (s), 1206 (s), 1159 (s), 1119 (s), 1076 (s), 1040 (w), 963 (m), 830 (s), 690 (m), 595 (m), 538 (w), 448 (w); ^1H NMR (400 MHz,