

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

NIR and CT luminescence spectra of [Yb(TFN)(S-BINAPO)] and [Yb(HFA)(S-BINAPO)] complexes



SPECTROCHIMICA ACTA

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HIGHLIGHTS

• The complexes [Yb(TFN)₃(S-BINAPO)] and [Yb(HFA)₃(S-BINAPO)] showed PL at low temperature.

- Complex [Yb(TFN)₃(S-BINAPO)] showed narrowed emission (half width ~6 nm) at 981 nm.
- The complex [Yb(HFA)₃(S-BINAPO)] showed strong emission peak at around 985 nm.
- Complex [Yb(TFN)₃(S-BINAPO)] showed CT emission at 412–463 nm.

ARTICLE INFO

Article history: Received 21 December 2013 Received in revised form 24 March 2014 Accepted 29 March 2014 Available online 6 April 2014

Keywords: NIR luminescence Yb(III) complex BINAPO CT transitions f-f transitions

Introduction

Lanthanide luminescence has numerous important applications in optoelectronic devices, phosphorescent devices, anion sensing, protein recognition, immunoassays, etc. [1–4]. Chiral as well as

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GRAPHICAL ABSTRACT

NIR PL Spectra of $[Yb(TFN)_3(S-BINAPO)]$ (a) and CT luminescence of $[Yb(TFN)_3(S-BINAPO)]$ (b). The complex, $[Yb(TFN)_3(S-BINAPO)]$ showed narrowed emission peak (half width ~6 nm) at around 981 nm at low temperature.



ABSTRACT

The complexes $[Yb(TFN)_3(S-BINAPO)](TFN = 4,4,4-trifluoro-1(2-napthyl)-1,3-butanedione) (complex 1) and <math>[Yb(HFA)_3(S-BINAPO)](HFA = hexafluoroacetylacetonate) (complex 2) were synthesized, characterized. The absorption as well as PL spectra have been studied. The complex <math>[Yb(TFN)_3(S-BINAPO)]$ showed narrowed emission peak (half width ~6 nm) at around 981 nm in addition to several emission peaks in NIR (near infrared) region. The complex $[Yb(HFA)_3(S-BINAPO)]$ showed strong emission peak at around 985 nm. The charge transfer luminescence of $[Yb(TFN)_3(S-BINAPO)]$ was also observed at 412–463 nm. © 2014 Elsevier B.V. All rights reserved.

luminescent lanthanide complexes are significant for their applications in material as well as biological sciences. Highly emissive and enantiopure lanthanide complexes have been used as cellular imaging and reactive probes by their interactions with DNA [5,6]. Population inversion in 4f orbitals in Ln(III) complexes is a great benefit in the development of organic chelate laser and plastic optical fiber applications [7–11]. Luminescences of Yb complexes in 3d–4f and energy transfer processes have been reported [12,13]. Luminescence from lanthanide ions in metal complexes are very sensitive to solvents coordinated to the metal centers.

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Scheme 1. Schematic diagram of (a) $[Yb(TFN)_3(S-BINAPO)]$ and (b) $[Yb(HFA)_3(S-BINAPO)]$.

The quenching of the luminescence due to the excited state relaxation through solvent molecules usually observed in case of lanthanide complexes. Introduction of the suitable bulky neutral ligand in a neutral lanthanide tris-(β -diketonato) complex can replace the solvent molecules from the coordination sphere resulting in improved luminescence as well as photophysical properties [14]. A comprehensive strategy to boost the luminescence of lanthanide complexes has been reported recently [15]. Phosphine oxide ligands can produce antisymmetrical structures that promote faster radiation rates because coordination of phosphine oxide moiety (1) prevents coordination of water or solvent molecules and (2) lowers vibrations ($P=0:1125 \text{ cm}^{-1}$) [16]. For this purposes β -diketonato ligands with chiral BINAPO (1,1'-binapthyl phosphine oxide) ligand were chosen. The complexes [Yb(TFN)₃ (S-BINAPO)](TFN = 4,4,4-trifluoro-1(2-napthyl)-1,3-butanedione) (complex 1) and [Yb(HFA)₃(S-BINAPO)](HFA = hexafluoroacetylacetonate) (complex 2) were synthesized (Scheme 1), characterized and their absorption as well as PL spectra have been studied.

Materials and methods

Materials

Ytterbium acetate monohydrate (99.9%), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (HFA) were purchased from Wako Pure Chemical Industries Ltd. 4,4,4-Trifluoro-1(2-napthyl)-1,3-butanedione (TFN) was purchased from Aldrich Chemical Co. BINAP was purchased from Wako Pure Chemical Industries Ltd. All chemicals and reagents were of analytical grade and used as received.

PL measurements

Solid state NIR (near infrared) PL spectra of the complexes were measured at low temperatures using a line of He–Cd laser as excitation source (at 325 nm). The visible PL spectra were measured by a spectrofluorophotometer (Shimadzu Corp., model RF-5301) using Xenon lamp as an excitation source.

Synthesis and characterization of the BINAPO and metal complexes

The S-BINAPO ligand was prepared by oxidation of BINAP [17] with H_2O_2 in THF at 0 °C for 12 h. The ligand was characterized by IR, NMR and elemental analysis. ¹H NMR (acetone d₆, TMS) peaks were obtained at δ 6.63 (d, 2H), δ 6.77 (t, 2H), δ 7.30–7.36

(m, 8H), δ 7.38–7.50 (m, 12H), δ 7.79–7.87 (q, 4H), δ 7.88–7.91(d, 2H) and δ 7.93–7.96(d, 2H) ppm. The elemental analysis of *S*-BINAPO ligand was performed; found C, 80.72%; H, 4.89% and calculated for C₄₄H₃₂O₂P₂, C, 80.75%; H, 5.03%.

Synthesis of [Yb(TFN)₃(S-BINAPO)] and [Yb(HFA)₃(S-BINAPO)]

Yb(HFA)₃ and Yb(TFN)₃ were synthesized by dissolving ytterbium acetate monohydrate in ethanol in a beaker and then adding slowly the ethanol solution of HFA or TFN with stirring in an ice bath (\sim 1:3 M ratio) according to the previous method [14]. An acetone solution (100 mL) containing Yb(HFA)₃ or Yb(TFN)₃ and BINAPO ligand (1:1 M ratio) was refluxed at \sim 50 °C for 10 h with continuous stirring to obtain a clear solution of desired complexes [Yb(HFA)₃(S-BINAPO)] and [Eu(TFN)₃(S-BINAPO)], respectively. In each case, the resulting mixture was concentrated and hexane was added to it, which gave crystalline precipitate. For an example synthesis of [Yb(TFN)₃(S-BINAPO)] is given here. [Yb(TFN)₃]·2H₂O (5 g, 5 mmol) was dissolved in 100 mL acetone in a round bottom flask. Then (3 g, 5 mmol) of S-BINAPO was added to the above solution. A turbid mixture obtained was shaken and a clear solution was obtained in a few min. This solution was refluxed for 10 h. The resulting mixture was concentrated and hexane was added. A white yellow crystalline solid obtained was filtered and dried in air (% yield, 60%). Elemental analyses for the following complexes were performed, results are as provided below: Calculated for, C₉₀H₅₆O₈₋ F₉P₂Yb, [Yb(TFN)₃(S-BINAPO)], %H, 3.38, %C, 64.68; found, %H 3.58, %C, 64.65; Calculated for, C₅₉H₃₅O₈F₁₈P₂Yb·C₆H₁₄, [Yb(HFA)₃ (S-BINAPO)] C₆H₁₄, %H, 3.22, %C, 50.86; found, %H 2.80, %C, 50.70; The ESI-MS data were collected for [Yb(HFA)₃(S-BINAPO)] and [Yb(TFN)₃(S-BINAPO)]complexes. For [Yb(HFA)₃(S-BINAPO)], *m* = 1449, *m*/*z* 1242, [1449-hfa]⁺; *m*/*z* 1896, [1449-hfa+BINAPO]⁺ and [Yb(TFN)₃(S-BINAPO)], m = 1623, m/z 655, BINAPO+H⁺; m/z1358, [M-TFN]⁺; *m*/*z* 2012, [M-TFN+BINAPO]⁺ were obtained.

Results and discussion

BINAPO ligand and metal complexes have been synthesize and characterized by elemental analyses, mass spectra and NMR. We previously have reported the X-ray structure of [Yb(HFA)₃ (S-BINAPO)], a square antiprism (SAP) structure was found [14]. Yb(III) has the most unique absorption among the rare earth series. The unique f-f transitions of Yb(III) from ground state ${}^{2}F_{7/2}$ to excited state ²F_{5/2} are split by the crystal field into four and three doubly degenerate sublevels, respectively. This is magnetically allowed $(\Delta J = 1)$ transition of Yb(III). For the Yb(III) complexes within f^{13} electronic configuration, three absorption bands have been observed at around 930 nm, 960 nm and 975 nm [6]. It has been found that if the absorption spectrum is taken in acetone then all the bands are well resolved for Yb(III) complex [6]. Absorption spectra of the complexes (1 and 2) have been measured in acetone. As shown in Fig. 1 three absorption bands were observed at 937, 957 and 975 nm for the complex 1. Absorption spectra showed only few transitions from ground ${}^{2}F_{7/2}$ to the excited ${}^{2}F_{5/2}$ levels



Fig. 1. Absorption spectra of complex [Yb(TFN)₃(S-BINAPO)] in acetone.

due to crystal field splitting (Fig. S1). However, multiple CD components in the complexes ascended from the ligand field splitting within the ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transitions of the Yb(III) chromophores [14]. These are several transitions from four Kramers doublets of the ground ${}^{2}F_{7/2}$ states to three of the excited ${}^{2}F_{5/2}$ states [14].

Fig. 2 shows the PL spectra of Yb(TFN)₃(S-3BINAPO) at 20 K. A sharp and strong NIR emission peak with narrowed band (half width ~6 nm) has been observed at around 981 nm. Three more strong peaks were also observed at 1000, 1016 and 1030 nm. In addition, small emission peaks were also observed at 947, 963, 1044, 1050 and 1061 nm. All these emissions are due to the transitions from the excited ${}^{2}F_{5/2}$ states to the ground ${}^{2}F_{7/2}$ states with in the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transitions of Yb(III) (Figs. 2 and 3). Fig. 4 shows the PL spectra of complex Yb(TFN)₃(S-3BINAPO) at 4 K, which is very similar to that observed at 20 K. As shown in Fig. 5, absorption spectra of complex 2 is similar to that observed for complex 1. three absorption bands are also observed approximately at 938. 960 and 976 nm due to the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transitions of Yb(III). For the complex [Yb(HFA)₃(S-BINAPO)] a strong and relatively broad emission band compared to that found for [Yb(TFN)₃(S-3BINAPO)] has been observed at 4 K as well as 20 K at around 985 nm (Figs. 6 and 7) corresponding to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transitions of Yb(III). In addition, few small emission peaks were also observed at 810, 855, 925, 1105 and 1140 nm. The emissions peaking at 925, 1105 and 1140 nm also originated from the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transitions. The emission peaks detected at 810 and 855 nm may have some contribution from charge transfer transitions. The broad emission band (half width ${\sim}80\,\text{nm})$ observed at 985 nm for the complex [Yb(HFA)₃(S-BINAPO)] may be due to the considerable reorganization of the charge density distribution around the metal ion. This reorganization is accompanied by an expansion of the metal-ligand bonds in the excited state, which gives rise to the observation of a relatively broad band.



Fig. 2. PL spectra of Yb(TFN)₃(S-3BINAPO) at 20 K.



Fig. 4. PL spectra of Yb(TFN)₃(S-3BINAPO) at 4 K.



Fig. 5. Absorption spectra of complex [Yb(HFA)₃(S-BINAPO)] in acetone.



Fig. 6. PL spectra of Yb(HFA)₃(S-3BINAPO) at 20 K.



Fig. 3. Schematic diagram showing four major transitions from excited ${}^{2}F_{5/2}$ states to ground ${}^{2}F_{7/2}$ states (1, 2, 3, 4 represents ground state levels and 1', 2', 3' are excited state levels).



For the complex [Yb(TFN)₃(*S*-BINAPO)] the visible luminescence spectra at 390–410 nm excitations were also recorded in acetone (Fig. 8). When excited at 390 nm three peaks were observed at 412, 434 and 458 nm. Excitations at 398 and 400 nm provided two emission peaks for each at 436 and 455 nm (Fig. 8). A broad peak centering at 463 nm was observed corresponding to 400 nm excitation. Yb(III)(4f¹³) is an ion for which charge transfer (CT) luminescence can be expected [18,19]. In this ion, the only excited 4f state, ${}^{2}F_{5/2}$, is located around 10,000 cm⁻¹ above the ground state ${}^{2}F_{7/2}$. Because of the large energy difference between the charge transfer state and the highest excited 4f state, the charge transfer luminescence in Yb(III) can be observed [20]. In our present case the violet-blue region emissions (412–463 nm) are



Fig. 8. PL spectra of [Yb(TFN)₃(S-BINAPO)] excitation at 390 nm (blue–), 398 nm (red–), 400 nm (green–), 410 nm (violet–). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 9. Excitation spectra of [Yb(TFN)₃(*S*-BINAPO)] excitation at 434 nm (blue–), 454 nm (red–). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

due to the CT transition from ligand to Yb(III) 4f levels (${}^{2}F_{5/2}$ or ${}^{2}F_{7/2}$). The CT transitions may involve a considerable reorganization of the charge density distribution around the Yb(III) ion. This reorganization is accompanied by an expansion of the metal-ligand bonds in the excited state, which gives rise to the observation of large Stokes shifts and broad luminescence bands in visible region for the [Yb(TFN)₃(S-BINAPO)] [20]. The excitation spectra for the [Yb(TFN)₃(S-BINAPO)] were measured in acetone. Broad and similar excitation peaks were observed at 398 and 399 nm when monitored at 434 and 454 nm respectively (Fig. 9).

Conclusion

The complexes $[Yb(TFN)_3(S-BINAPO)](TFN = 4,4,4-trifluoro-1 (2-napthyl)-1,3-butanedione) (complex 1) and <math>[Yb(HFA)_3(S-BINAP-O)](HFA = hexafluoroacetylacetonate) (complex 2) were synthesized, characterized and their absorption as well as PL spectra were studied. The complex <math>[Yb(TFN)_3(S-BINAPO)]$ showed narrowed emission peak (half width ~6 nm) at around 981 nm in addition to several emission peaks in NIR region at low temperature. The complex $[Yb(HFA)_3(S-BINAPO)]$ showed strong emission peak at around 985 nm (half width ~80 nm). The CT luminescence for the $[Yb(TFN)_3(S-BINAPO)]$ was observed in 412–463 nm region. The broadening of some PL peaks may be due to the considerable reorganization of the charge density distribution around the Yb(III) ions accompanied by an expansion of the metal–ligand bonds in the excited state.

Acknowledgement

Professors Yanagida Shozo of Osaka University, Japan and Yasuchika Hasegawa of Hokkaido University, Japan are thankfully acknowledged for their cooperation.

Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.03.109.

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