



Synthesis, crystal structure and effect of deuterated solvents and temperature on visible and near infrared luminescence of N4-donor Schiff base lanthanide complexes



Shuo Chen, Rui-Qing Fan, Song Gao, Xinming Wang, Yu-Lin Yang*

Department of Chemistry, Harbin Institute of Technology, No. 92, Xidazhi Street, Nangang District, Harbin 150080, PR China

ARTICLE INFO

Article history:

Received 7 October 2013
Received in revised form
31 December 2013
Accepted 2 January 2014
Available online 15 January 2014

Keywords:

Lanthanides
Schiff base
Luminescence
Deuterated solvents
Temperature

ABSTRACT

A series of lanthanide complexes $[\text{LnL}(\text{NO}_3)_3] \cdot \text{CH}_3\text{CN}$ [$\text{Ln} = \text{Ce}$, (**1•Ce**); Nd, (**2•Nd**); Tb, (**3•Tb**); Dy, (**4•Dy**); Ho, (**5•Ho**); Er, (**6•Er**); Tm, (**7•Tm**); Yb (**8•Yb**)] have been synthesized by the reaction of N4 chelate ligand *N,N'*-bis(2-pyridinylmethylene)cyclohexane-1,2-diamine (**L**) with lanthanide salts. Photoluminescence spectra of complexes **2•Nd**, **3•Tb**, **4•Dy**, and **8•Yb** show the strong characteristic luminescence from visible to near infrared (NIR) region. Further, the singlet state ($32,467 \text{ cm}^{-1}$) and the lowest triplet ($23,202 \text{ cm}^{-1}$) energy level of **L** are calculated, indicating that the energy transfer from **L** to Tb^{3+} ion is more effective than that to Dy^{3+} ion. An extended work is developed to discuss on the effect of deuterated reagent and temperature on luminescent properties of **3•Tb** and **8•Yb**.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Over the past couple of decades, luminescent lanthanide complexes have attracted a great deal of attention due to their potential applications in organic light-emitting diodes (OLEDs) [1–3], luminescent molecular probes [4–8] and telecommunication [9]. Most trivalent lanthanide ions feature long-lived and line-like emission bands at the characteristic wavelengths from visible to near infrared region. However, for these lanthanide ions, because of the parity-forbidden nature of *f–f* transitions, the absorption coefficients ($\epsilon = 1\text{--}10 \text{ M}^{-1} \text{ cm}^{-1}$) are normally very low and the emission rates are slow [10–12]. In order to overcome this shortcoming, a number of elements can be deduced from the classical “antenna effect” theory [13–15]. To enhance the emissions, the organic chromophores are often employed to transfer the absorbed energy efficiently to the lanthanide ions. Among the different candidates, multidentate Schiff base ligands are usually selected as ideal antenna for encapsulation of Ln^{3+} ions. Such functional ligands may help to improve the luminescent properties by shielding the lanthanide centers from the outside solvent environment [16,17]. Therefore, the absorbed energy could transfer effectively from the chromophores to Ln^{3+} ions and the minimization of non-radiative processes of the Ln(III) can be realized [18,19]. Besides, the low-energy excited states are facile to quench by nearby O–H, N–H, and C–H oscillators [20,21]. Therefore, it is desirable to avoid or decrease the number of these groups close to the lanthanide center [22]. The deuterated reagents are adoptable as the

most direct and effective method [23–27], which lead to better visible and NIR luminescence properties.

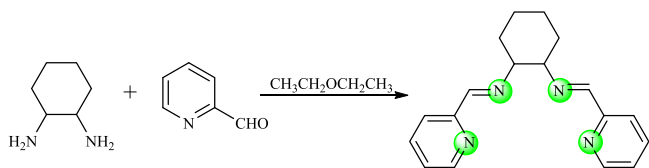
Previously, Jones et al. have reported some salen type ligands to stabilize Ln^{3+} centers and provide the antenna for lanthanide luminescence [28–32]. Our group have documented the synthesis, luminescence properties of several complexes incorporating the bis(imino)pyridyl Schiff base ligand [33–36]. As part of our ongoing interest in the photophysical properties of Schiff base lanthanide complexes, we describe here the visible and NIR luminescence of lanthanide complexes utilizing N4-donor **L** as the chromophore (Scheme 1). As shown in Scheme 2, eight lanthanide complexes $[\text{LnL}(\text{NO}_3)_3] \cdot \text{CH}_3\text{CN}$ ($\text{Ln} = \text{Ce}$, (**1•Ce**); Nd, (**2•Nd**); Tb, (**3•Tb**); Dy, (**4•Dy**); Ho, (**5•Ho**); Er, (**6•Er**); Tm, (**7•Tm**); Yb (**8•Yb**)) are obtained possessing a bispyridine(cyclohexane) backbone. Complexes **3•Tb** and **4•Dy** display Ln-centered strong green and yellowish-green luminescence, complexes **2•Nd** and **8•Yb** show the strong characteristic luminescence in near-infrared region. The energy transfer mechanisms are discussed according to the singlet state and triplet state energy level. The luminescence properties influenced by the deuterated reagents and temperature have been studied in detail.

2. Experimental section

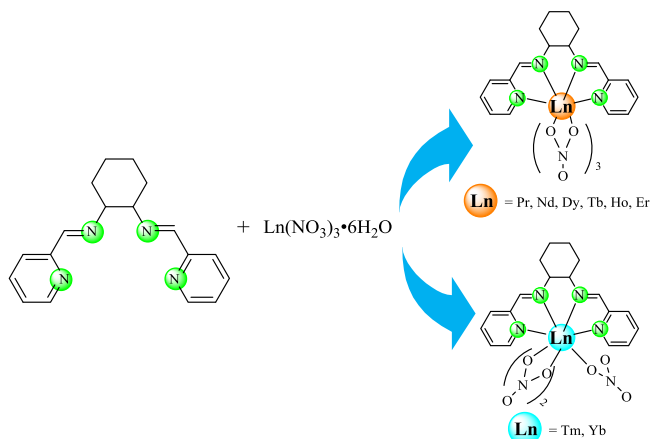
2.1. Materials and measurements

All reagents were analytical grade from commercial sources and were used directly without any further purification. 1,2-diaminocyclohexane and pyridine-2-carboxaldehyde were purchased from Aldrich Co., Ltd and Acros Co., Ltd, respectively. Hydrous lanthanide

* Corresponding author. Tel./fax: +86 451 86413710.
E-mail address: ylyang@hit.edu.cn (Y.-L. Yang).



Scheme 1. Synthetic procedure of N4-donor ligand **L**.



Scheme 2. Synthetic routes of lanthanide complexes **1–8**.

nitrate ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$ and Yb) were purchased from Ji Nan Henghua Sci. & Tec. Co. Ltd. (Shandong, China). Solvents for reaction and photophysical studies were dried and freshly distilled under dry nitrogen gas before use. The deuterated solvents (> 99.8%) were deaerated before the photoluminescence measurements. ^1H NMR (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance-400 spectrometer using $\text{Si}(\text{CH}_3)_4$ as an internal standard at room temperature. Elemental analysis for C, H, and N were performed on a Perkin-Elmer 2400 automatic analyzer. Fourier transform (FT)-IR spectra were measured on a Perkin-Elmer Spectrum 100 FT-IR Spectrometer with samples prepared as KBr discs. UV spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer. Powder X-ray thermogravimetric studies were performed in air. Variable-temperature X-ray powder diffraction (VT-XRPD) patterns were obtained using a PANalytical X-ray diffractometer, equipped with monochromated $\text{Cu K}\alpha$ radiation 40 mA, 40 kV. Each powder pattern was recorded in the $5\text{--}50^\circ\text{C}$ range (2θ) from RT to 800°C with a step of 0.02° and a counting time of 0.4 s. The temperature ramp between two consecutive temperatures was $10^\circ\text{C min}^{-1}$. The solid-state and solution photoluminescence analyses were carried out on an Edinburgh FLS920 fluorescence spectrometer in the range of 200–1600 nm. The visible and NIR detectors as well as the lifetime setup are red-sensitive photomultiplier (type r928) and InSb detector. Phosphorescence analyses were carried out at 77 K with an Oxford Optistat DN™ cryostat (with liquid nitrogen filling). For the solid samples, the absolute quantum yields have been measured by integrating sphere.

2.2. Syntheses

2.2.1. *N,N'*-bis(2-pyridylmethylene)cyclohexane-1,2-diamine (**L**)

A mixture of pyridine-2-carboxaldehyde (1.9 mL, 20 mmol) and 1,2-diaminocyclohexane (1.2 mL, 10 mmol) was stirred in anhydrous diethyl ether (20 mL) at room temperature for 24 h. After filtering, the ivory-white precipitate was collected and washed with cold ether. Pure product was obtained in 72% yield (2.14 g) by recrystallization from *n*-hexane. UV (CH_2Cl_2 , 25°C): λ_{max} (nm) =

201, 235, 265; FT-IR (KBr, cm^{-1}): $\nu = 3049$ (m, $\nu_{\text{py, C-H}}$), 3007 (m), 2934 (s), 2885 (s), 1645 (vs, $\nu_{\text{C=N}}$), 1567 (s), 1467 (s), 1078 (m), 993 (m), 791 (s), 620 (s); ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 8.57$ (d, $J = 4.4$ Hz, 2H, CH=N), 8.34 (s, 2H, Py-H), 7.90 (t, $J = 7.6$ Hz, 2H, Py-H), 7.69 (t, $J = 7.6$ Hz, 2H, Py-H), 7.26 (t, $J = 5.2$ Hz, 2H, Py-H), 3.55 (q, $J = 5.2, 7.6$ Hz, 2H, Cy-CH), 1.90–1.54 ppm (m, 8 H, Cy- CH_2); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 161.45, 154.64, 149.24, 136.43, 124.46, 122.31, 73.56, 32.73, 24.36$; elemental analysis calcd for **L** [$\text{C}_{18}\text{H}_{20}\text{N}_4$ (292.38)]: C, 73.94; H, 6.89; N, 19.16%. Found: C, 73.98; H, 6.92; N, 19.09%.

2.2.2. $[\text{LnL}(\text{NO}_3)_3] \cdot \text{CH}_3\text{CN}$ (**1–8**) [$\text{Ln} = \text{Ce}$ (**1**•Ce), Nd (**2**•Nd), Tb (**3**•Tb), Dy (**4**•Dy), Ho (**5**•Ho), Er (**6**•Er), Tm (**7**•Tm), and Yb (**8**•Yb)]

All complexes were prepared with the similar procedure as described below. A solution $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) in CH_3OH (10 mL) was added to a solution of **L** (146.2 mg, 0.5 mmol) in CH_3OH (10 mL). The mixture was stirred under reflux temperature for 6 h. After cooling to the room temperature, a white precipitate formed which was collected by filtration. Single crystal suitable for X-ray structure determination could be obtained by means of recrystallization in CH_3CN .

[CeL(NO₃)₃]·CH₃CN (1•Ce) Yield: 461.7 mg (70%); UV (CH_3OH , 25°C): λ_{max} (nm) = 210, 231, 270; FT-IR (KBr, cm^{-1}): $\nu = 3416$ (m, br), 2942 (m), 2850 (w), 2254 (w), 1654 (s, $\nu_{\text{C=N}}$), 1602 (vs), 1476 (s), 1378 (s), 1306 (s), 1154 (s), 1028 (m), 1012 (s), 814 (w), 778 (s), 412 (m); elemental analysis calcd for **1** [$\text{C}_{20}\text{H}_{23}\text{N}_8\text{O}_9\text{Ce}$ (659.58)]: C, 36.42; H, 3.52; N, 16.99%. Found: C, 36.36; H, 3.65; N, 16.83%.

[NdL(NO₃)₃]·CH₃CN (2•Nd) Yield: 477.8 mg (72%); UV (CH_3OH , 25°C): λ_{max} (nm) = 213, 231, 274; FT-IR (KBr, cm^{-1}): $\nu = 3416$ (m, br), 2942 (m), 2862 (w), 2254 (w), 1654 (s, $\nu_{\text{C=N}}$), 1602 (vs), 1496 (s), 1386 (s), 1306 (s), 1164 (s), 1100 (m), 1020 (s), 814 (w), 778 (s), 420 (m); elemental analysis calcd for **2** [$\text{C}_{20}\text{H}_{23}\text{N}_8\text{O}_9\text{Nd}$ (663.70)]: C, 36.19; H, 3.49; N, 16.88%. Found: C, 36.29; H, 3.52; N, 16.74%.

[TbL(NO₃)₃]·CH₃CN (3•Tb) Yield: 461.3 mg (68%); UV (CH_3OH , 25°C): λ_{max} (nm) = 210, 233, 274; FT-IR (KBr, cm^{-1}): $\nu = 3416$ (m, br), 2942 (m), 2862 (w), 2254 (w), 1654 (s, $\nu_{\text{C=N}}$), 1604 (vs), 1496 (s), 1386 (s), 1304 (s), 1154 (s), 1020 (m), 814 (w), 788 (s), 420 (m); elemental analysis calcd for **3** [$\text{C}_{20}\text{H}_{23}\text{N}_8\text{O}_9\text{Tb}$ (678.38)]: C, 35.41; H, 3.42; N, 16.52%. Found: C, 35.36; H, 3.37; N, 16.63%.

[DyL(NO₃)₃]·CH₃CN (4•Dy) Yield: 450.1 mg (66%); UV (CH_3OH , 25°C): λ_{max} (nm) = 210, 232, 275; FT-IR (KBr, cm^{-1}): $\nu = 3408$ (m, br), 2942 (m), 2862 (w), 2254 (w), 1654 (s, $\nu_{\text{C=N}}$), 1602 (vs), 1486 (s), 1386 (s), 1306 (s), 1282 (s), 1154 (m), 1020 (s), 814 (w), 412 (m); elemental analysis calcd for **4** [$\text{C}_{20}\text{H}_{23}\text{N}_8\text{O}_9\text{Dy}$ (681.96)]: C, 35.23; H, 3.40; N, 16.43%. Found: C, 35.11; H, 3.57; N, 16.20%.

[HoL(NO₃)₃]·CH₃CN (5•Ho) Yield: 417.5 mg (61%); UV (CH_3OH , 25°C): λ_{max} (nm) = 211, 232, 276; FT-IR (KBr, cm^{-1}): $\nu = 3406$ (m, br), 2947 (m), 2862 (w), 2254 (w), 1652 (s, $\nu_{\text{C=N}}$), 1592 (vs), 1481 (s), 1388 (s), 1306 (s), 1285 (s), 1160 (m), 1105 (s), 1017 (s), 818 (w), 784 (s), 418 (m); elemental analysis calcd for **5** [$\text{C}_{20}\text{H}_{23}\text{N}_8\text{O}_9\text{Ho}$ (684.39)]: C, 35.10; H, 3.39; N, 16.37%. Found: C, 35.05; H, 3.33; N, 16.38%.

[ErL(NO₃)₃]·CH₃CN (6•Er) Yield: 508.2 mg (74%); UV (CH_3OH , 25°C): λ_{max} (nm) = 210, 231, 282; FT-IR (KBr, cm^{-1}): $\nu = 3420$ (m, br), 2951 (m), 281 (w), 2253 (w), 1651 (s, $\nu_{\text{C=N}}$), 1599 (vs), 1477 (s), 1386 (s), 1305 (s), 1283 (s), 1160 (m), 1028 (s), 812 (w), 417 (m); elemental analysis calcd for **6** [$\text{C}_{20}\text{H}_{23}\text{N}_8\text{O}_9\text{Er}$ (686.72)]: C, 34.98; H, 3.38; N, 16.32%. Found: C, 34.95; H, 3.34; N, 16.34%.

[TmL(NO₃)₃]·CH₃CN (7•Tm) Yield: 358.0 mg (52%); UV (CH_3OH , 25°C): λ_{max} (nm) = 210, 232, 283; FT-IR (KBr, cm^{-1}): $\nu = 3398$ (m, br), 2942 (m), 2854 (w), 2254 (w), 1646 (s, $\nu_{\text{C=N}}$), 1602 (vs), 1502 (s), 1386 (s), 1298 (s), 1154 (s), 1100 (m), 1020 (s), 814 (w), 788 (s), 420 (m); elemental analysis calcd for **7** [$\text{C}_{20}\text{H}_{23}\text{N}_8$

Download English Version:

<https://daneshyari.com/en/article/5400241>

Download Persian Version:

<https://daneshyari.com/article/5400241>

[Daneshyari.com](https://daneshyari.com)