



## Linear and nonlinear optical properties of Ln–Zn heteronuclear complexes from a Schiff base ligand containing 8-hydroxyquinoline moiety



Ling Chen<sup>a</sup>, Cheng Yan<sup>a</sup>, Bin-Bin Du<sup>a</sup>, Kai Wu<sup>a</sup>, Lu-Yin Zhang<sup>a</sup>, Shao-Yun Yin<sup>a</sup>, Mei Pan<sup>a,b,\*</sup>

<sup>a</sup> MOE Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

<sup>b</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

### ARTICLE INFO

#### Article history:

Received 27 June 2014

Received in revised form 3 July 2014

Accepted 6 July 2014

Available online 8 July 2014

#### Keywords:

Schiff base ligand

NIR

Nonlinear optical properties

### ABSTRACT

Starting from a Schiff base ligand containing 8-hydroxyquinoline moiety, namely, 3,3'-(1E,1'E)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene) diquinolin-8-ol (H<sub>2</sub>PBIQ), five heteronuclear Ln(III)–Zn(II) complexes (([Eu<sub>2</sub>Zn(PBIQ)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, **1**), ([Tb<sub>2</sub>Zn(PBIQ)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, **2**), ([Gd<sub>2</sub>Zn(PBIQ)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, **3**), ([Nd<sub>2</sub>Zn(PBIQ)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, **4**), and ([Yb<sub>2</sub>Zn(PBIQ)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, **5**) were obtained. Due to the low energy level resided in the excited state, the Schiff base ligand can sensitize near infrared emitting Ln(III) ions (Nd and Yb), while visible light emitting Eu and Tb ions cannot be excited. Instead, nonlinear optical properties were observed in Eu/Tb–Zn heteronuclear complexes.

© 2014 Elsevier B.V. All rights reserved.

Schiff base type ligands are most widely applied in coordination chemistry, due to their variety of chemical structures and versatile physicochemical properties [1–4]. Coordination complexes obtained from Schiff base ligands have been the focus of recent studies because of their potential applications in various chemical and biological areas such as organic synthesis, catalyst, antimicrobial and antifungal agents, as well as linear and nonlinear optical properties [5–7]. On the other hand, due to its specific spatial and electronic structures, 8-hydroxyquinoline (Q) has been extensively used in the preparation of coordination complexes, especially for potential applications in light emitting materials and OLED devices [8–10]. Therefore, the introduction of 8-hydroxyquinoline moiety into Schiff base might result in new type of ligands to assemble coordination complexes, for better understanding the energy transfer process and tuning the optical properties.

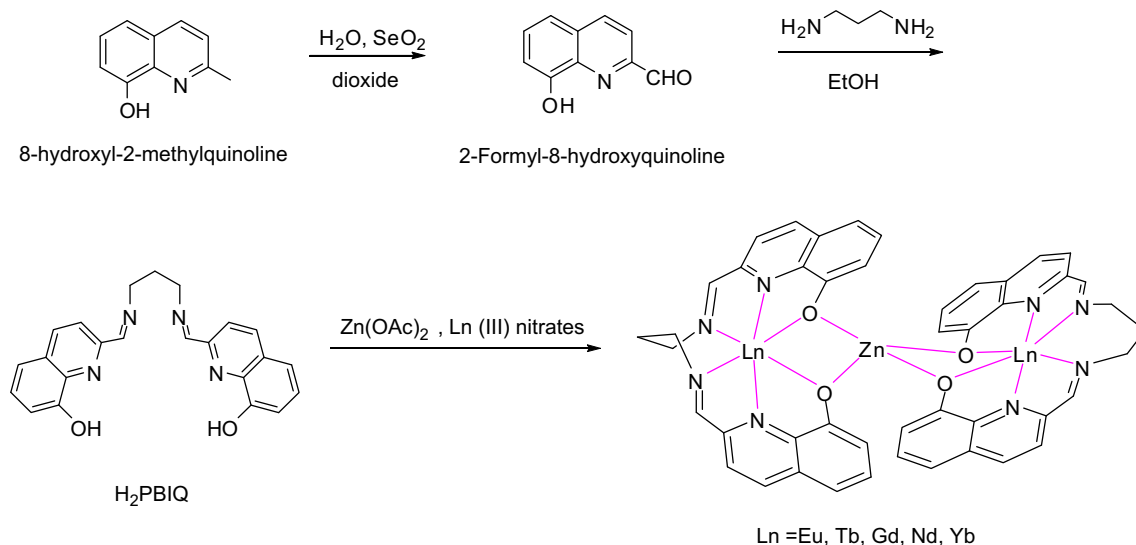
Herein, a new Schiff base ligand containing 8-hydroxyquinoline moiety, namely, 3,3'-(1E,1'E)-(propane-1,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diquinolin-8-ol (H<sub>2</sub>PBIQ) was designed (Scheme 1). The co-assembly of H<sub>2</sub>PBIQ with Zn(OAc)<sub>2</sub> and Ln(III) nitrates (Ln = Eu, Tb, Gd, Nd, Yb) afforded a series of isomorphous hetero-trinuclear complexes: ([Eu<sub>2</sub>Zn(PBIQ)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, **1**), ([Tb<sub>2</sub>Zn(PBIQ)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, **2**), ([Gd<sub>2</sub>Zn(PBIQ)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, **3**), ([Nd<sub>2</sub>Zn(PBIQ)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, **4**), and ([Yb<sub>2</sub>Zn(PBIQ)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, **5**) [11–13]. The complexes are crystallized in C<sub>2</sub>/c space group, in which the coordination unit contains two PBIQ<sup>2-</sup> ligands, two Ln(III) metal centers and one Zn(II) metal center,

therefore forming a hetero-trinuclear structure. The coordination sphere of Ln(III) ions in these complexes is ten-coordinated, in which the hexadentate PBIQ<sup>2-</sup> ligand affords four N and two O atoms, and simultaneously, four O atoms from two nitrate anions help to satisfy the {N<sub>4</sub>O<sub>6</sub>} bi-capped square antiprism coordination atmosphere, which has altogether 10 vertices and 16 triangular faces. Meanwhile, the Zn(II) center is encapsulated in a 4-coordinating tetrahedron geometry with four bridging O atoms from 8-hydroxyquinoline groups in two different PBIQ<sup>2-</sup> ligands (Scheme 1, Fig. 1a). The coordination units are further stacked together by abundant hydrogen bonds and only minor cavities can be observed along c direction (Fig. 1b).

The UV–vis absorption spectra of the complexes in DMSO solution are similar, and we only take the spectrum of complex **1** as an example (Fig. S1). As we can see, the major absorption peaks at 270 and 298 nm can be attributed to singlet–singlet π–π\* transitions of the heterocyclic groups on the ligand. While the longest absorption band of the complex extends into 500 nm, in accordance with its dark-red color, which is also characteristic of a Schiff-base complex. Furthermore, the solid state absorption spectra of heteronuclear complexes **1–3** are shown in Fig. S2. We can see that the complexes in the solid state have long absorption bands extending above 500 nm, which is also due to the specific electronic structure in the Schiff base ligand. The triplet energy state of the PBIQ<sup>2-</sup> ligand is estimated to be around 16,500 cm<sup>-1</sup> according to the phosphorescence spectra of complex **3** measured at 77 K as shown in Fig. S3. It can be noted that the triplet energy level of the Schiff base ligand lies well below the energies of the main emitting levels of <sup>5</sup>D<sub>0</sub> for Eu<sup>3+</sup> (17,500 cm<sup>-1</sup>) and <sup>5</sup>D<sub>4</sub> for Tb<sup>3+</sup> (20,400 cm<sup>-1</sup>), therefore it cannot sensitize these visible light emitting Ln<sup>3+</sup> ions. Instead, due to the coordination effect, the ligand based S<sub>1</sub> → S<sub>0</sub> luminescence is

\* Corresponding author at: School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China.

E-mail address: [panm@mail.sysu.edu.cn](mailto:panm@mail.sysu.edu.cn) (M. Pan).

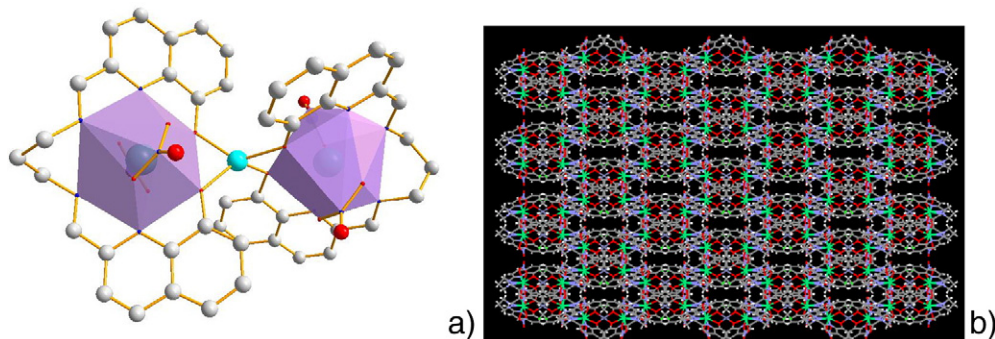


**Scheme 1.** Structure and syntheses of the ligand H<sub>2</sub>PBIQ and complexes 1–5 (coordinated nitrate anions are omitted for clarity).

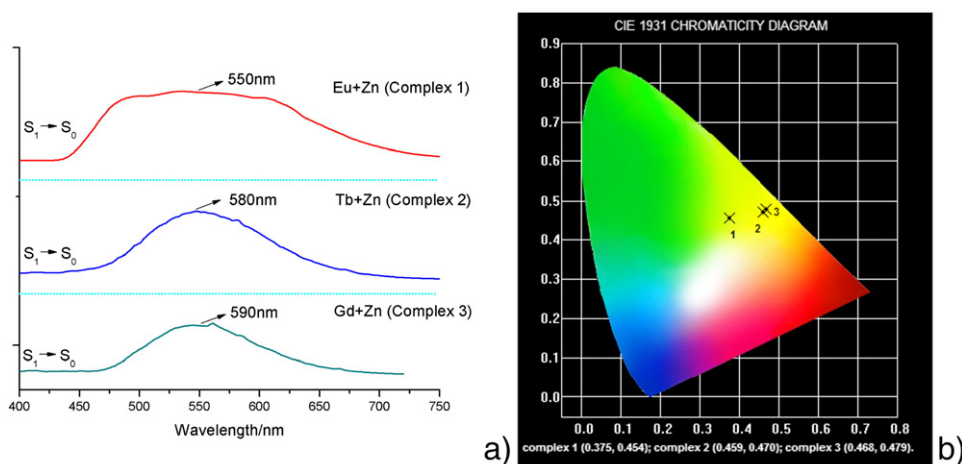
intensified. Meanwhile, the emission contours of complexes 1–3 show obvious difference. As we can see, Eu–Zn complex 1 has the widest emission wavelength covering from 450 to 700 nm, Tb–Zn complex 2 from 475 to 670 nm, while Gd–Zn complex 3 emits within 470 to 650 nm (Fig. 2a). Therefore, the calculated CIE coordinates of the three complexes fall into (0.375, 0.454), (0.459, 0.470), and (0.468, 0.479), respectively, extending from near-green to pure-yellow region (Fig. 2b). The luminescent lifetimes of the three complexes detected at 550,

580, and 590 nm were 0.179, 0.131, and 0.326 ns for complexes 1–3, respectively. The obvious difference in the ligand-based luminescent lifetime might suggest distinct energy transfer rate or progress in these three complexes.

On the other hand, the low energy state resided in the ligand is suitable for energy transfer to the emitting levels of <sup>4</sup>F<sub>3/2</sub> of Nd<sup>3+</sup> and <sup>2</sup>F<sub>5/2</sub> of Yb<sup>3+</sup> energy levels around 10,000 cm<sup>-1</sup>. Therefore, NIR emissions at ~900, 1050, 1340 nm (<sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>9/2</sub>, <sup>4</sup>I<sub>11/2</sub>, <sup>4</sup>I<sub>13/2</sub> transitions for Nd<sup>3+</sup>)



**Fig. 1.** The coordination structure of complexes 1–5 showing the coordination environment of Ln(III) (encapsulated in purple polyhedron) and Zn(II) (in cyan) metal centers (a, H atoms omitted for clarity), and packing states along *c* direction (b).



**Fig. 2.** Solid state luminescence of heteronuclear complexes 1–3 at room temperature: emission spectra (a) and calculated CIE coordinates (b).

Download English Version:

<https://daneshyari.com/en/article/1301748>

Download Persian Version:

<https://daneshyari.com/article/1301748>

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