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



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#### ABSTRACT

Starting from a Schiff base ligand containing 8-hydroxyquinoline moiety, namely, 3,3'-(1E,1'E)-(propane-1,3diylbis(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.

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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*2/*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,

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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  $\pi$ - $\pi$ \* 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  $PBIQ^{2-}$  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  $Eu^{3+}$  (17,500 cm<sup>-1</sup>) and  ${}^{5}D_{4}$  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  $S_1 \rightarrow S_0$  luminescence is

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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 life-time 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  ${}^{4}F_{3/2}$  of Nd<sup>3+</sup> and  ${}^{2}F_{5/2}$  of Yb<sup>3+</sup> energy levels around 10,000 cm<sup>-1</sup>. Therefore, NIR emissions at ~900, 1050, 1340 nm ( ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}, {}^{4}I_{11/2}, {}^{4}I_{13/2}$  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).



Fig. 3. Solid state luminescence of heteronuclear complexes 4-5 at room temperature.

#### Table 1

Photophysical properties of complexes 1-5.

Sample	Emission center/nm	$\tau/ns$ or $\mu s$
Complex $1$ (Zn + Eu)	550	0.179 ns
Complex $2(Zn + Tb)$	580	0.131 ns
Complex $3(Zn + Gd)$	590	0.326 ns
Complex $4(Zn + Nd)$	870, 906, 1054*(detected	1.1 µs
	for emission lifetime), 1341	
Complex <b>5</b> $(Zn + Yb)$	980	2.5 µs



and 980 nm ( ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transition for Yb<sup>3+</sup>) were observed for complexes **4** and **5** (Fig. 3). Meanwhile, based on the results of time-resolved luminescent experiments, luminescent decay curves can be fitted mono-exponentially with time constants of microseconds for the two complexes (1.1 µs for **4** and 2.5 µs for **5**). Therefore, the intrinsic quantum yields  $\Phi_{Ln}$  can be estimated by  $\Phi_{Ln} = \tau_{obs} / \tau_{0}$ , where  $\tau_{obs}$  is the observed emission lifetime and  $\tau_{0}$  is the "neutral lifetime" of Nd<sup>3+</sup> (0.25 ms) and Yb<sup>3+</sup> ions (2.0 ms), respectively (see Table 1) [14]. For the two NIR emitting complexes,  $\Phi_{Ln}$  values of 0.6 and 0.1% are obtained, respectively.

The NLO properties of heteronuclear complexes 1 and 2 were measured by Z-scan technique using a tunable nanosecond laser system (532 nm, 21 ps, 0.39 µJ). Firstly, the NLO absorption components were evaluated by Z-scan experiment under an open aperture (OA) configuration, as shown in Fig. 4. The curves demonstrate a negative nonlinear absorption for both two complexes. It is obvious that the theoretical curves (red line) qualitatively reproduce well the general pattern of observed experimental data (black and blue dots). This fact suggests an effective third order characteristic for experimentally detected NLO effects. The two-photon absorption coefficients  $\beta$  of complexes **1** and **2** were calculated to be  $6 \times 10^{-11}$  and  $3.5 \times 10^{-11}$  m/W, respectively. Furthermore, the NLO refractive effects of the complexes were assessed by dividing the normalized Z-scan data obtained under closed aperture (CA) configuration by the normalized Z-scan data obtained under the open aperture (OA) configuration. From the experimental results, complex 1 does not show obvious NLO refractive effect, while complex 2 has a second-order hyperpolarizabilities  $\gamma$  calculated to be  $-9.5\times10^{-18}\,m^2/W,$ which means that the compound has a self-defocusing property.

In summary, the coordination of Ln(III) ions with a Schiff base ligand results in a series of isomorphous d–f heteronuclear complexes, with



Fig. 4. Nonlinear absorption and refractive Z-scan curves of heteronuclear complexes 1 and 2.

either intensified red emission from the ligand or sensitized NIR emission from Ln(III) ions. Furthermore, nonlinear optical properties were also observed in these d–f heteronuclear complexes. These properties provide potential applications in such areas as optical amplification, medical diagnostic probe, and OLED devices.

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### Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.inoche.2014.07.009. These data include MOL files and InChiKeys of the most important compounds described in this article.

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- [10] N.M. Shavaleev, H. Adams, J. Best, R. Edge, S. Navaratnam, J.A. Weinstein, Inorg. Chem. 45 (2006) 9410.
- [11] Preparation of the ligand: 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). A mixture of 8-hydroxyl-2-methylquinoline (4 g, 25 mmol), selenium dioxide (3.5 g, 31 mmol), H<sub>2</sub>O (3 mL), 1,4-diethylene dioxide (300 mL) was stirred at 80 °C for 24 h under the protection of nitrogen. After cooling, the mixture was filtered and the filtrate evaporated. The solid was purified by silica-gel column chromatography (developing solvent-petroleum ether:ethyl acetate, 95:5, v/v) to yield pure yellow needle crystal of 2-Formyl-8-hydroxyquinoline. Yield = 90%; <sup>1</sup>H NMR (400 MHz, CDCI<sub>3</sub>): δ 10.25 (s, 1H), 8.35 (d, J = 8.5 Hz, 1H), 8.18 (s, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.31 (d, J = 7.7 Hz, 1H). 2-Formyl-8-hydroxyquinoline (0.173 g, 1 mmol), 1,3-diaminopropane (42 μL, 0.5 mmol) were added to 20 mL ethanol and stirred at room temperature. After two hours, the reaction mixture was filtered and then got the final ligand H<sub>2</sub>PBIQ. Selected IR data (KBr pellet, cm<sup>-1</sup>): 3401.79 (OH), 1645.26 (C=N). The ligand was not stable by itself, so no further characterization was performed.
- [12] Preparations of the complexes: A solution of the ligand H<sub>2</sub>PBIQ (0.05 mmol, 19 mg) in dichloromethane (2 mL) was added to the bottom of a tube. And then, in turn, 10 mL mixture solution (dichloromethane: ethanol, v/v = 50:50,) and 2 mL solution of  $Eu(NO_3)_3$ · 6H<sub>2</sub>O (0.05 mmol, 23 mg) in ethanol were carefully added into the tube. After laying at room temperature for a month, red needle-like crystals of **1** suitable for single crystal diffraction were obtained from the middle liquid layer. Anal. Calcd. (%) for C<sub>46</sub>H<sub>36</sub>N<sub>12</sub>O<sub>16</sub>Eu<sub>2</sub>Zn (**1**·0.5CH<sub>2</sub>Cl<sub>2</sub>): C, 39.51; H, 2.627; N, 11.95. Found (%): C, 39.72; H, 2.829; N, 11.30. Complexes **2**–5 were obtained by the same synthetic method as that for **1**. Complex **2**: Anal. Calcd. (%) for C<sub>46</sub>H<sub>36</sub>N<sub>12</sub>O<sub>16</sub> Tb<sub>2</sub>Zn (**2**·0.5CH<sub>2</sub>Cl<sub>2</sub>): C, 38.82; H, 2.599; N, 11.69. Found (%): C, 38.82; H, 2.851; N, 10.97. Complex **4** Anal. Calcd. (%) for C<sub>46</sub>H<sub>36</sub>N<sub>12</sub>O<sub>16</sub> Md<sub>2</sub>Zn: C, 40.42; H, 2.65; N, 12.30. Found (%): C, 40.3; H, 2.778; N, 11.62. Phase purity of the complexes was confirmed by PXRD as shown in Fig. S4.
- [13] Crystal data for 1:  $C_{46}H_{36}N_{12}O_{16}Eu_2Zn$  (1·CH<sub>2</sub>Cl<sub>2</sub>), Mr = 1467.09, monoclinic, space group C2/c, a = 21.4663(4) Å, b = 12.4115(2) Å, c = 19.1299(2) Å, \beta = 97. 148(1)°, V = 5057.15(14), Z = 4, T = 150 K, D<sub>calcd</sub>. = 1.927 g.cm<sup>-3</sup>,  $\mu$  = 19. 771 mm<sup>-1</sup>, R = 0.0443(3081), wR<sub>2</sub> = 0.1202(3899) and GOF = 0.877. The crystal structures were solved by direct methods using SHELXS-97 program and refined on F<sup>2</sup> by full-matrix least squares using SHELXL-97 program. All non-H atoms were refined anisotropically while all H atoms were placed in geometrically idealized positions.
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