



# Effects of the substituting groups and proton abstraction on the nonlinear optical properties of heteroleptic bis-tridentate Ru(II) complexes

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## ABSTRACT

The second-order nonlinear optical (NLO) properties have been carried out on a series of Ru(II) complexes with different 4'-substituted terpyridine derivatives and the tridentate ligand 2,6-bis(benzimidazole-2-yl)pyridine by using density functional theory (DFT). The introduction of different substituents enhances the static first hyperpolarizabilities in various degrees. Time-dependent density functional theory (TD-DFT) calculations indicate that the additional metal-to-ligand charge transfer (MLCT) transition, which is vectorially opposite to the intraligand charge transfer (ILCT) transition, could contribute to the smaller  $\beta_{vec}$  in species with electron-withdrawing groups compared to ones with electron-donating groups. The stepwise deprotonation brings about a change in electron density of the benzimidazole moiety and finally makes the moiety turn to be as donor, which subsequently leads to an efficient second-order NLO switching. For the species **3** with electron-donating group, the  $\beta_{vec}$  value of the mono-deprotonated system is 49.9 and 11.1 times as small as that of its diprotonated and fully deprotonated ones.

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## 1. Introduction

As new types of chromophores, organometallic and coordination complexes with enhanced nonlinear optical (NLO) properties have continued to be in the limelight over the past two decades [1,2]. Compared to organic molecules, organometallic and coordination complexes offer additional flexibility by varying the metal, its oxidation state, the ligand environment and the geometry [3–9]. Moreover, they exhibit large and fast nonlinearities by introducing new NLO active charge-transfer transitions between the metal and the ligand, such as metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT) and metal-to-metal/intervalence charge transfer (MM/IVCT) [1,10,11]. These advantages of metal complexes are conducive to efficiently switching the second-order NLO responses at the molecular level, which could provide the basis for a range of molecular-scale devices. If the NLO responses of a compound are reversibly tuned between 'on' and 'off' states, it will be a promising candidate as NLO switching. Furthermore, the reversible NLO switching would come true by a simple controllable perturbation. So far, several switching schemes at the molecular level, involved with metal complexes, have been explored. The

more elegant perturbation depends on isomerisation or tautomerization of molecules [12] that causes change in the nature and/or degree of conjugation between electron donor and acceptor. Another appealing scheme is based on lowering the donor capacity of the electron-rich fragment of a typical donor-acceptor (D-A) species by oxidation or protonation, and the acceptor capacity by reduction or deprotonation [8,9,13,14].

Ru(II/III) polypyridyl complexes that exhibit excellent electrochemical and optical (linear and nonlinear) properties are of great current interest in the field of photoelectric functional materials [15–18]. It is worth noting that the coordination of chelating groups to metal center could generate push-pull systems, and such systems may be beneficial to produce large NLO responses. Many studies concerning NLO property have been reported for Ru(II/III) polypyridyl complexes. The most studied type is the well-known Ru(II) tris-bipyridine complexes. The ligand structures have been modified, substituted with both electron-donating and electron-withdrawing groups [18–22], to obtain the maximization of the first hyperpolarizability  $\beta$  value that governs quadratic NLO response at the molecular level. Compared with bipyridine complexes, structurally more appealing terpyridine (tpy) Ru(II/III) complexes are also promising to become the candidates with excellent NLO properties [23–25] because of the high binding affinity of tpy with transition metals and the facile functionalization of the 4'-position of tpy [26,27]. Baitalik et al. recently

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synthesized and characterized a new series of Ru(II) mono-terpyridine complexes  $[(\text{H}_2\text{pbbzim})\text{Ru}(\text{tpy}-\text{X})]^{2+}$ , where  $\text{H}_2\text{pbbzim} = 2,6\text{-bis}(\text{benzimidazole-2-yl})\text{pyridine}$  and  $\text{tpy}-\text{X} = 4'$ -substituted terpyridine derivatives [28]. The report points out that this class of complexes not only has the unique photophysical and redox properties, but also displays wonderful color changes because of the stepwise deprotonation of two benzimidazole N–H fragments (Fig. 1) [29] while in presence of excess anions. What draws our attention most, however, is that the stepwise deprotonation process is fully reversible [28,29], which could provide the possibility in the application of proton driven molecular switches.

A number of reports have investigated the spectroscopic, electrochemical and luminescence properties of Ru(II) complexes containing  $\text{H}_2\text{pbbzim}$  and terpyridine derivatives, but a systematic study on NLO properties of these complexes is lacking. So how are their NLO responses? With enhanced emission quantum and excited-state lifetimes, will the molecular first hyperpolarizability  $\beta$  also be effectively enhanced after the substitution of tpy by electron-withdrawing groups? For organic chromophores containing benzimidazole, the influence of deprotonation on NLO properties is so apparent that the range of change in  $\beta$  value is from  $14 \times 10^{-30}$  esu (protonation) to  $1189 \times 10^{-30}$  esu (deprotonation) according to the theoretical calculation results [30]. Then how about Ru(II) complexes with benzimidazole based on the tridentate ligand  $\text{H}_2\text{pbbzim}$ ? Will the deprotonation bring the same changes? Keeping these questions in mind, we have carried out a detailed theoretical study to discuss the second-order NLO properties of a series of heteroleptic bis-tridentate Ru(II) complexes  $[(\text{H}_n\text{pbbzim})\text{Ru}(\text{tpy}-\text{X})]^{n+}$  ( $n = 2,1,0$ ) featuring five different end groups on the tpy moiety, from strong donor (complex **3**:  $\text{X} = \text{Ph}-\text{NMe}_2$ ) to strong acceptor (complex **5**:  $\text{X} = \text{Ph}-\text{NO}_2$ ) (Fig. 2). Among them, complexes  $\mathbf{1}^{2+}$  ( $\text{X} = \text{H}$ ),  $\mathbf{2}^{2+}$  ( $\text{X} = \text{Ph}-\text{CH}_3$ ) and  $\mathbf{4}^{2+}$  ( $\text{X} = \text{Ph}-\text{CHO}$ ), together with the mono-protonated and fully deprotonated forms, have been reported in the experiment [28].

## 2. Computational details

All calculations in this work were carried out using the Gaussian 09W program package [31]. The geometries of all complexes were optimized with no symmetry constraint using Becke's 3-parameter hybrid exchange functional combined with Lee-Yang-Parr's gradient-corrected correlation functional (B3LYP) [32,33]. Basis sets of LANL2DZ containing relativistic effects for Ru<sup>II</sup> and 6-31G\* for C, N, O and H were applied. Based on the optimized geometries, vibrational frequencies were calculated to verify that each of the geometries is the most stable. At the same level of theory, Natural bond orbital (NBO) analysis was performed with the NBO 3.1 program [34] as implemented in Gaussian. To obtain a more intuitive description of the band assignments of the electron spectra and the trends in the NLO behavior of the studied complexes, UV–vis absorption spectra were calculated by time-dependent density functional theory (TD-DFT) method. Both PBE0 and CAM-B3LYP functionals were applied to find a reliable approach for our calculations.

The static first hyperpolarizability tensors of all the complexes were calculated by finite field (FF) method with a field frequency of

0.0010 a.u.. The FF method is widely applied to investigate NLO as this methodology can be used in concert with the electronic structure method to compute  $\beta$  [35]. In this work, B3LYP and CAM-B3LYP functionals were employed to study  $\beta$  (Table S3). The results indicate that both functionals give consistent trends on the first hyperpolarizabilities. However, the B3LYP greatly overestimates the  $\beta$  value, just as previously reported [36]. The basis set effect on the  $\beta$  values is also compared. Based on the conclusion as explained in Supporting information, we will employ the CAM-B3LYP/6-31g\* (LANL2DZ basis set for metal ion) method to investigate the static first hyperpolarizabilities of all the studied complexes.

The static first hyperpolarizability  $\beta_{vec}$ , which is the vector component of  $\beta$  along the dipole moment direction, was calculated using the following equation [35]:

$$\beta_{vec} = \sum_{i=1}^3 \frac{\mu_i \beta_i}{|\mu|} \quad (1)$$

Here,  $\mu$  is the ground-state molecular dipole moment and  $\beta_i$  is defined as:

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{j \neq i} [(\beta_{ijj} + \beta_{jjj} + \beta_{jji})] \quad i, j = x, y, z \quad (2)$$

## 3. Results and discussion

### 3.1. Geometry structures

In the present paper, all the complexes are classified into five groups by the kind of the substituents: species **1** ( $\text{X} = \text{H}$ ), species **2** ( $\text{X} = \text{Ph}-\text{CH}_3$ ), species **3** ( $\text{X} = \text{Ph}-\text{NMe}_2$ ), species **4** ( $\text{X} = \text{Ph}-\text{CHO}$ ) and species **5** ( $\text{X} = \text{Ph}-\text{NO}_2$ ). As a result of the presence of the crystal data of the diprotonated complex with  $\text{Ph}-\text{CH}_3$ , we first compare the optimized structure of species **2**, hereinto, the diprotonated complex is named system  $\mathbf{2}^{2+}$ , the mono-deprotonated one is system  $\mathbf{2}^+$ , and the fully deprotonated one is system **2**. Different protonated forms of the other species are named in the same way. The geometric parameters for the species **2** are given in Table 1 with the comparison of experimental values [28] and the atom labels is shown in Fig. 3. The calculation offers a distorted octahedral configuration and the two kinds of ligands are in planes perpendicular to each other, which can be seen from the angle subtended at the metal ion in the optimized molecular structure (Fig. 3). As shown in Table 1, the abstraction of proton from the benzimidazole moiety has a significant effect on the configuration of the studied complexes. Compared with the diprotonated system, both the Ru–N(pyridine) distances to the tpy ligand and the Ru–N(benzimidazole) distances are shortened after deprotonation. And the angles N(2)–Ru–N(4) are decreasing slightly ( $154.7^\circ(\mathbf{2}^{2+}) > 154.3^\circ(\mathbf{2}^+) > 154.1^\circ(\mathbf{2})$ ) whereas the other angles N(6)–Ru–N(8) are increasing in a certain extent ( $156.3^\circ(\mathbf{2}^{2+}) < 157.0^\circ(\mathbf{2}^+) < 157.8^\circ(\mathbf{2})$ ). The same changing trend in the other four species could be observed with the stepwise deprotonation. The variation in geometry suggests that the abstraction of

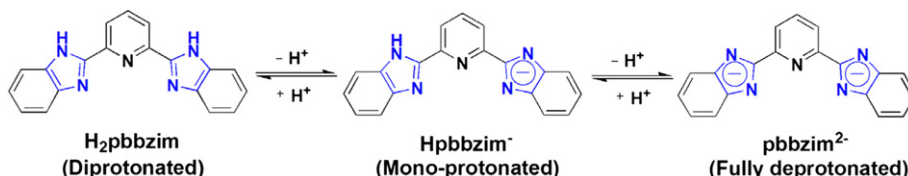


Fig. 1. Stepwise and reversible deprotonation of  $\text{H}_2\text{pbbzim}$  unit.

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