



# Computational study: How redox affect the nonlinear optical properties of donor substituted heteroleptic bis-tridentate Ru(II) complexes?

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## ABSTRACT

Donor substituted heteroleptic bis-tridentate Ru(II) complexes with different deprotonated forms exhibit larger alterations of the first hyperpolarizabilities in oxidized process and are promising to become redox-switchable nonlinear optical (NLO) molecular materials. For systems with diprotonated form, the  $\beta_{\text{vec}}$  value of the two-electron-oxidized system  $\mathbf{1}^{32+}$  is 5.3 and 178.6 times as large as those of the reduced parent  $\mathbf{3}$  and the one-electron-oxidized system  $\mathbf{3}^+$  according to the DFT–FF results. For systems with mono-protonated form, the oxidization of the deprotonated benzimidazole anion is more helpful to enhance the  $\beta_{\text{vec}}$  value because of the increasing  $\beta_x$  component. For systems with fully deprotonated form, the largest ratio of  $|\beta_{\text{vec}}(\mathbf{1}^+)|/|\beta_{\text{vec}}(\mathbf{1}^0)|$  of the system without substituent is about 13.2 due to the dominant off-diagonal tensor  $\beta_{zxx}$ . And the time-dependent density functional theory (TDDFT) results indicate that the charge transfer transition of the first excited state displays an indispensable role for larger off-diagonal tensor. Finally, the calculated frequency-dependent  $\beta$  results exhibit a small dispersion effect at the low-frequency region.

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## 1. Introduction

Switchable nonlinear optical (NLO) molecular materials have attracted considerable attention because of their novel and interesting applications in optoelectronic technologies [1,2]. Generally speaking, the NLO behavior could be switched by reversibly modifying the capacity of the donor/acceptor and the nature of the  $\pi$ -conjugated bridge. Among them, the more appealing scheme is based on lowering the donor/acceptor capacity of a typical donor–acceptor (D–A) species by oxidation/reduction or protonation/deprotonation [3–6]. In order to obtain an effective switching, the molecule must be stable in two (or more) states that offer different NLO responses.

Organotransition metal complexes have always been chosen as the candidates of multifunctional NLO materials due to their excellent electrochemical and optical (linear and nonlinear) properties [2,7–9]. Especially, metal-based redox, which reversibly switches different types of NLO phenomena, is becoming the promise in switchable-NLO field for its easy acquirement [1–4]. Coe et al. [10,11] have reported a range of V-shaped metal-based chromophores with reversible Ru<sup>III/II</sup> waves. Results suggest that those complexes possess the potential as redox-switchable NLO

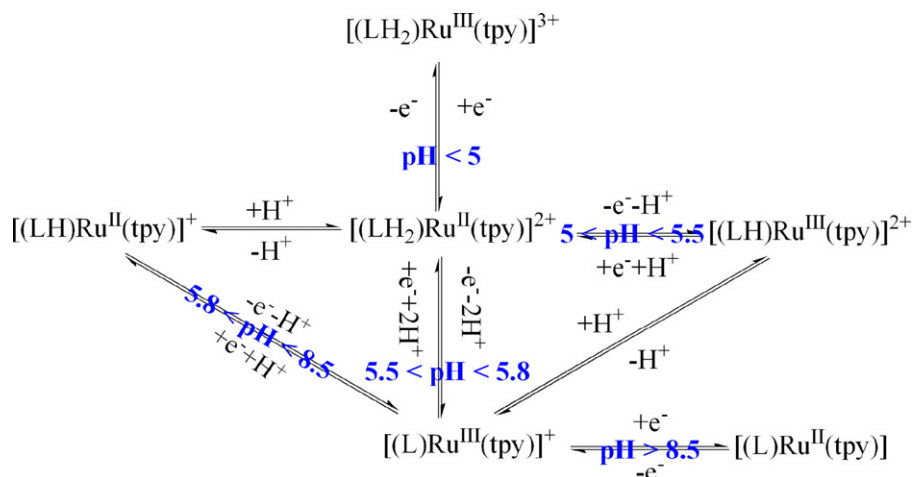
chromophores because of their large first hyperpolarizabilities  $\beta$  that governs quadratic NLO response at the molecular level. Most intriguing, these metallochromophores show two-dimensional (2D) NLO character because of the dominant off-diagonal  $\beta_{zyy}$  tensor. Compared to traditional 1D species, multidimensional NLO chromophores, which show more than one charge transfer (CT) directions, could offer better nonlinearity/transparency trade-off. Therefore, multidimensional NLO molecules have been considered as candidates for optimization of NLO responses [10–15].

Tridentate ligand 2,6-bis(benzimidazole-2-yl)pyridine (LH<sub>2</sub>) and its derivatives have been coordinated to transition metals for structure and property investigations [16–21]. This kind of ligands is so attractive that they can offer a combination of moderate  $\pi$ -acceptor pyridine nitrogen and  $\pi$ -donor imidazole nitrogen. Moreover, the presence of one or more dissociable N–H proton makes it possible to tune the spectroscopic and redox properties by deprotonation. Ruthenium complexes with the tridentate ligand LH<sub>2</sub> have been studied on their photophysical and electrochemical properties [20–23]. Results show that both the absorption spectra and the redox potentials are strongly pH-dependent in consequence of the ligand based completely reversible protonation or deprotonation processes. According to the work taken by Mondal et al. [22], the approximate numerical dependency of deprotonation and redox process of a set of Ru monoterpyridine (tpy) complexes are summarized and shown in Scheme 1. Among them, both the diprotonated and fully deprotonated forms have been isolated as solid crystals and demonstrated to show excellent electrochemical behaviors. Although the cyclic voltammogram

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**Scheme 1.** pH dependence of electron transfer, proton transfer and proton coupled electron transfer processes in acetonitrile:water (1:4, v/v). From Ref. [22].

involving the mono-deprotonated forms has not been apparently involved, pH dependent absorption spectral changes do clearly indicate the existence of mono-deprotonated intermediate.

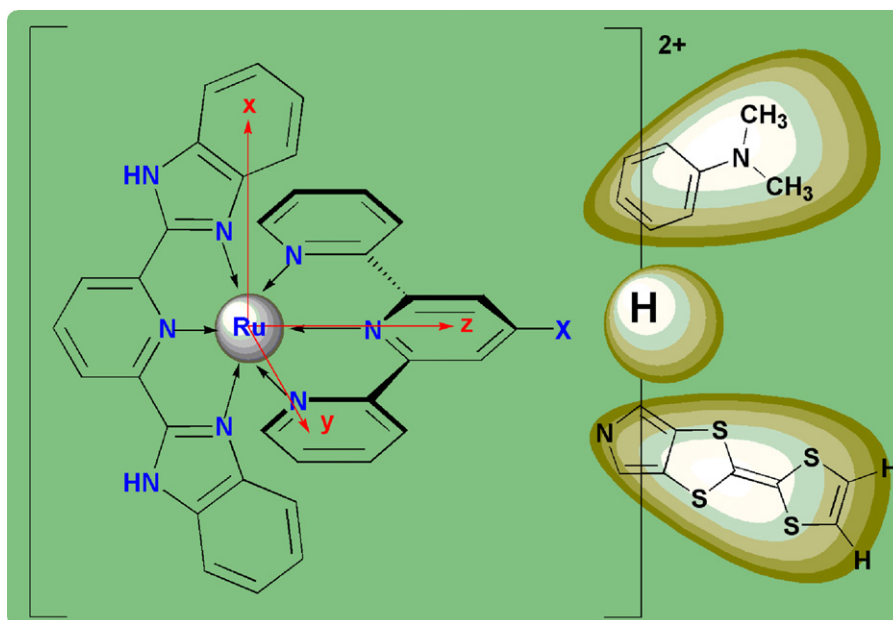
Prior to this work, we studied the NLO properties on a family of complexes  $[(LH_2)Ru^{II}(tpy-X)]^{2+}$  with different electron-donating and electron-withdrawing groups together with their deprotonated forms [24]. We found that the introduced group X acts as an donor in the CT process, therefore the addition of electron-donating moiety is good for larger CT and larger NLO coefficient. Tetrathiafulvalene (TTF) unit is not only an efficient  $\pi$ -electron donor but also an excellent redox-active center due to the possibility of reversible stepwise oxidation forming stable radical cation and dication species ( $TTF \leftrightarrow TTF^{\bullet+} \leftrightarrow TTF^{2+}$ ) [25]. Redox-switchable NLO properties on organic and organometallic TTF systems have been studied both experimentally and theoretically, and the static first hyperpolarizability  $\beta$  substantially is changed by the oxidized TTF species [15,26,27]. Thus, we further study the relationship between redox states and second-order NLO responses for complexes  $[(LH_2)Ru^{II}(tpy-X)]^{2+}$  couple with deprotonation, where X points to H (species **1**), Ph-NMe<sub>2</sub> (species **2**) and monopyrrolo-TTF

(species **3**) (Fig. 1). There are two reasons that we choose the monopyrrolo-TTF moiety instead of simple TTF unit as substituent. One is that the basic skeleton of the substituted tpy ligand is kept the same and the branch is along the coordinate axis. The other is that this kind of organics has been synthesized and the cyclic voltammetry shows two pairs of reversible redox waves [25,28,29].

## 2. Computational details

All calculations in this work were performed using the Gaussian 09W program package [30]. The structures of all complexes were optimized at the (U)B3LYP/6-31G\* level (LANL2DZ basis set for Ru atom) without symmetry constraint. And vibrational frequency calculations were carried out to verify that the obtained structures are local minima on the potential energy surface.

The static first hyperpolarizability tensors of all complexes were calculated by finite field (FF) method with a field frequency of 0.0010 a.u. The FF method is broadly applied to investigate the NLO response as this methodology can be used in concert with the electronic structure method to compute  $\beta$  [31]. In the present paper,



**Fig. 1.** Structural formulas of complexes coupled with substituents.

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