



Nonlinear optical properties of rhenium(I) complexes: Influence of the extended π -conjugated connectors and proton abstraction



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ABSTRACT

The photoinduced proton-coupled electron transfer chemistry is very crucial to the development of nonlinear optical (NLO) materials with large first hyperpolarizability contrast. We have performed a systematic investigation on the geometric structures, NLO switching, and simulated absorption spectra of rhenium(I) complexes via density functional theory (DFT). The results show that the first hyperpolarizabilities (β_{vec}) increase remarkably with further extending of the organic connectors. In addition, the solvent leads to a slight enhancement of the hyperpolarizability and frequency dependent hyperpolarizability. Furthermore, the proton abstraction plays an important role in tuning the second-order NLO response. It is found that deprotonation not only increases the absolute value of β_{vec} but also changes the sign of β_{vec} from positive to negative. This different sign can be explained by the opposite dipole moments. The efficient enhancement of first hyperpolarizability is attributed to the better delocalization of the π -electron system and the more obvious degree of charge transfer. Therefore, these kinds of complexes might be promising candidates for designed as proton driven molecular second-order NLO switching.

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1. Introduction

In recent years, the design and synthesis of non-linear optical (NLO) molecular materials have attracted considerable attention due to their unique applications in optical fiber, data storage, and signal processing [1–4]. Comparing with traditional organic chromophores, the transition metal molecules play important roles in NLO activities. Because they exhibit large and fast NLO activities by charge-transfer transitions between the metal and ligands [5–8]. The transition metal complexes Ru(II), Fe(II), Pt(II), Re(I) and Ni(II) have shown versatile second-order NLO properties [9–13]. For example, Ordronneau et al. have reported that the β value of the Re(I) dithienylethene complex increases about 5-fold through reversible photoisomerization process, which achieves a switchable NLO response [14]. Then, the effect of metal chelation on various push–pull ligands such as substituted pyridines [15], phenanthroline [16], and dithiolene [17] has been extensively studied. Especially, the substituted phenanthroline and pyridine ligands

show the excellent chelating ability [18]. When these ligands are coordinated to the metal center, the chelation prompts them to adopt plane arrangement, which is favorable for large second-order NLO response [19,20].

For metal complexes, they 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 [21,22]. To obtain the effective switching of the molecular first hyperpolarizability, the prerequisite is that a molecule must exist at least two stable states [23]. Specific methods including redox, protonation, and photocyclization have been employed to switch the NLO responses [24–26]. Among them, the more appealing schemes are redox and protonation, since they can lower the donor/acceptor capacity of the typical donor–acceptor significantly ($D-A$) [27,28].

Recently, series of Re(I) complexes were synthesized and investigated, in which the phenol unit is linked covalently to the tricarbonyl-(phenanthroline) (pyridine)rhenium(I) via a variable number of benzene rings spacers ($n=0-2$) [29], that is, $[\text{Re}(\text{phen})(\text{CO})_3(\text{py-phOH})]^+$ (phen = 1,10-phenanthroline; CO = carbonyl; py-phOH = phenolate–pyridine) (Fig. 1). Besides, the phenolate moieties of the Re(I) complexes can undergo reversible deprotonation–protonation processes, which provides

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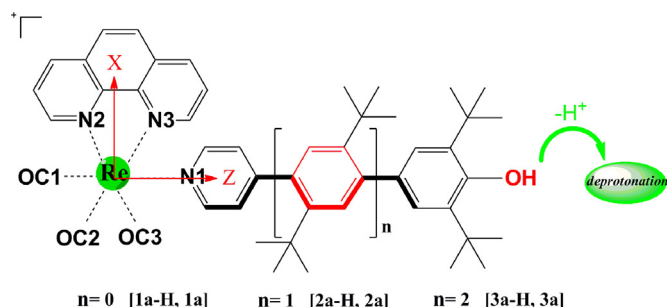


Fig. 1. The geometric structures of the studied complexes (**1a-H**, **2a-H**, and **3a-H** are the protonated complexes, while **1a**, **2a**, and **3a** are the deprotonated complexes).

the possibility for the molecular NLO switching. In the present work, the protonated forms are named as **1a-H** to **3a-H**, while the corresponding deprotonated forms are **1a-3a** (Fig. 1). We have also investigated the influence of π -conjugated connectors (by changing the number of benzene rings) on the second-order NLO response.

2. Computational details

All of the calculations were carried out using the Gaussian 09W program package [30]. It is well-known that B3LYP method shows good accuracy to optimize the geometries of the medium-sized molecules [31]. Thus, all complexes were optimized at the B3LYP/6-31G(d) (LANL2DZ basis set for Re ion) level without symmetry constraint. At the same level of theory, natural bond orbital (NBO) analysis was performed at the B3LYP/6-31+G(d)/LANL2DZ level. To further understand the bonding character of complexes, we evaluated the Wiberg bond index (WBI) using NBO analysis. The electrostatic potential (ESP) and electron density analysis was performed by Multiwfn 3.5 software [32]. The ESP was plotted using VMD 1.9.1 [33]. According to Ref. [34], the proton binding energy, ΔE_{H^+} , is defined as:

$$\Delta E_{H^+} = (E \{ \text{Re}(I)(\text{phen})(\text{CO})_3(\text{py} - \text{phO}) \} + ZPE \{ \text{Re}(I)(\text{phen})(\text{CO})_3(\text{py} - \text{phO}) \}) - (E \{ [\text{Re}(I)(\text{phen})(\text{CO})_3(\text{py} - \text{phOH})]^+ \} + ZPE \{ [\text{Re}(I)(\text{phen})(\text{CO})_3(\text{py} - \text{phOH})]^+ \}) \quad (1)$$

where $(E, ZPE) \{ \text{Re}(I)(\text{phen})(\text{CO})_3(\text{py} - \text{phO}) \}$ and $(E, ZPE) \{ [\text{Re}(I)(\text{phen})(\text{CO})_3(\text{py} - \text{phOH})]^+ \}$ are the electronic energies and zero-point energies of the optimized complexes, respectively. The static first hyperpolarizabilities of the studied complexes were calculated by analytical third energy derivatives, which are more efficient and less expensive [35,36]. For dipolar molecules, the first hyperpolarizability is generally related to the β_{vec} value, which is the vector component of β along the dipole moment direction and given by the following equation:

$$\beta_{\text{vec}} = \sum_{i=x,y,z} \frac{\mu_i \beta_i}{|\mu|} \quad (2)$$

where β_x , β_y , and β_z represent the components of the first hyperpolarizability tensor along x -, y -, and z -axis, respectively. Here, μ is the ground-state dipole moment, β_i is defined by the equation:

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

To check the consistency of results, we have calculated the first hyperpolarizabilities using three functionals, including hybrid exchange-correlation B3LYP, long-range corrected functionals LC-BLYP and CAM-B3LYP. The long-range corrected (LC) XC functional,

LC-BLYP [37,38] with a range-separating parameter μ of 0.47, furthermore, LC-BLYP contains 100% of HF exchange in the long-range limit. Among them, LC XC functionals have been shown to correct conventional DFT schemes for their shortsighted drawbacks [39]. The BLYP method is based purely on Kohn–Sham DFT formalism, combining the standard Slater local exchange functional with the exchange gradient-corrected Becke and the Lee–Yang–Parr correlation functional [40]. The CAM-B3LYP functional [41], which adds a long-range correction using the Coulomb-attenuating method and includes 19% and 65% of short- and long-range HF exchange with $\mu = 0.3$, is suitable to predict the molecular NLO properties of large systems. In addition, the PCM model has been used to examine the solvent effect on the first static hyperpolarizabilities and frequency-dependent hyperpolarizabilities.

In order to elucidate the origin of second-order NLO properties, we employed time-dependent density functional theory (TD-DFT) to describe the electronic spectra. The TD-DFT method is one of the most successful and extensively used methods to calculate the excitation energies in quantum chemistry owing to its efficiency and accuracy. To choose suitable calculated methods, the electron absorption spectrum of complexes **1a-H** and **2a-H** was simulated using TD-CAM-B3LYP and TD-PBE1PBE methods with 6-31+G(d) (LANL2DZ basis set for Re ion) basis set associated with the polarized continuum model (PCM) in acetonitrile solution (Table S1). According to the results, absorption spectrum of complex **1a-H** contains one high-energy electronic transition absorbing at 287 nm along with a low-energy electronic transition at 298 nm, which tally with the experiment result [29]. Similarly, absorption spectrum of complex **2a-H** contains one high-energy electronic transition absorbing at 284 nm along with a low-energy electronic transition at 299 nm. Thus, the TD-CAM-B3LYP functional was selected for the simulation of the absorption spectra of the studied complexes.

3. Results and discussion

3.1. Geometric and electronic structure

As shown in Fig. 1, the Re is coordinated by three carbonyl, one pyridine, and one phenanthroline ligand to form an almost perfect octahedral coordination polyhedron. The initial geometric structure of complex **2a-H** is derived from X-ray crystal data. The calculated geometric parameters of complex **2a-H** at the B3LYP/6-31G(d) level are in reasonable agreement with reported experimental data (Table 1). To obtain more accurate geometry, solvent effect has been taken into account in optimization and modeled using the polarized continuum model (PCM). We also optimized the geometrical structure of complex **2a-H** in the acetonitrile solution (Table 1). It can be clearly observed that the deviation of the calculated bond lengths ($\leq 0.002 \text{ \AA}$) and bond angles ($\leq 1.99^\circ$) for complex **2a-H** based on the B3LYP method in vacuum or acetonitrile solution is very small and negligible. Hence, the geometric structures and electronic properties of all complexes have been computed in vacuum at the B3LYP/6-31G(d) level with real frequency. The results show that both the (Re–N, Re–C) distances and (N–Re–N, N–Re–C, and C–Re–C) angles are slightly effected (in range of 0.001–0.019 \AA and $< 5^\circ$, respectively) during

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