Theoretical exploration of second-order nonlinear optical properties of mono- and bimetallic Pt(II) dithienylcyclopentene complexes: Ligands and photoisomerization effect

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1. Introduction

During the last two decades, compounds with large nonlinear optical (NLO) response have attracted extensive interest in view of their potential application involving optical computing, electro-optical devices as well as all-optical data processing technologies [1–6]. Since the earliest scientific publication reported the NLO properties of cis-1-ferrocenyl-2-(4-nitrophenyl)ethylene by Green et al. [7], organometallic complexes have emerged as a remarkable class of molecular NLO-phores owing to better thermal stability, ultrafast response times, stronger nonresonant responses and low dielectric constants in producing functional materials [8–12]. Besides, it has been demonstrated that the organometallic complexes have many additional electronic advantages over traditional organic counterparts on account of their low-energy charge-transfer transitions like metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), metal-to-metal/intervalence charge transfer (MM/IVCT) excitations and the electronic distribution modulated by redox switching of the metal centre. The fundamental researches on NLO materials have been paid more attention to pursue large NLO response. Meanwhile, the researches for metal complexes with switchable NLO properties have another important topic.

In recent years, the switchable properties of photochromic materials such as magnetic properties, linear and nonlinear optical properties have been extensive investigated owing to their widespread applications in photo-optical switching devices and optical memory media [13–17]. In order to obtain pronounced switching effect, the compounds must be stable in multistate that exhibit different NLO responses, high switching speed and reversibility in various practical applications. The switching of NLO properties can be altered by specific procedures including photoisomerization, oxidation/reduction and protonation/deprotonation [18–24]. Among them, the dithienylethene(DTE) as a classic photoswitching unit has been widely studied due to the remarkable low photo-fatigue and thermal stability [25–27]. The photochromic moieties undergo reversible process between open and closed forms by UV light irradiation and visible spectral ranges, accompanied by...
significant changes of electrochemical and NLO properties [28–30]. Moreover, a number of efforts have been devoted to theoretical investigations and synthesis of metal complexes with DTE-derived active component with desired NLO switchable properties [31–36]. The first example of zinc(II) DTE photochromic dipolar complexes have been reported by Aubert group [31]. They described that the \( \mu_0 \) values of closed-ring are larger than those of open-ring isomers. Samoc et al. synthesized a binuclear Ru(II) alkynyl complex with a diarylethene bridge, which shows six switchable states and possesses distinct NLO behaviors [36]. Additionally, the Pt(II) combined to DTE-based ligands complexes have been paid attention to their NLO properties by experiments or theoretical calculations [37–42]. Jacquemin with co-workers contributed a series of researches on the NLO properties of cyclometalated Pt(II) DTE-containing complexes. In 2014, they reported the first example of photochromic cyclometalated Pt(II) complexes as switchable NLO polymer films with better NLO contrast. The electron-donor group (D = NMe₂) introduction into Pt(II) complex can provide good second-order NLO response [39]. In addition, the novel cyclometalated Pt(II) (phppy) DTE-based complexes with sequential double nonlinear optical switch have been investigated in detail by the EFISH technique and theory. The values of \( \mu_0 \) for studied complexes are enhanced by protonation and then increased upon photocyclization owing to the longer charge-transfer distance and higher dipole moment [40]. A series of nonconjugated chroomatic Pt(II) complexes, synthesized two covalently linked bimetallic Pt(II) complexes, where the two metal fragments are diversely framing the same DTE core and the quadratic NLO properties were characterized via EFISH method. This work illustrates an enhanced photomodulation of the NLO response in the DTE closed form. The value of \( \mu_0 \) for complex Pt(II)-acetylide moieties connected to the reactive atoms is slightly larger than that previously reported monometallic Pt(II) complex in open form [41]. Recently, a series of functionalization Pt(II) complexes where the DTE unit is connected at the perimeter of the central benzene of the ligand were also synthesized and characterized in both solution and thin films. The remarkable enhancement of the second-order NLO response upon ring-closing is due to the extended \( \pi \)-delocalization and decrease of the HOMO–LUMO gap. However, the substitution of perfluorocyclopentene group does not clearly affect the quadratic NLO activity [42]. The development of these materials may be expected to result in novel switchable NLO applications. In previous work, our group systematically studied the NLO properties of a series of Pt(II) (acetylacetonate) (2,2’-thiophenylpyridine) derivatives. It is mainly discussed that multiple relationships with the number of thiophene rings and tuning electron-withdrawing substituents accompanied with adjustment of NLO response [43]. Recently, Gamez et al. have synthesized a series of novel Pt(II) complexes with photoresponsive DTE ligands and assessed the properties of potential biomedical properties [44]. Intriguingly, the notable geometry changes of these Pt(II) DTE-based complexes from nonconjugated form(open-ring) to conjugated state (closed-ring) will result in the switchable NLO responses. Stimulated by the excellent previous works, we carried out density functional theory (DFT) to research the electronic structures, electronic absorption spectra and the quadratic hyperpolarizabilities values of the Pt(II)-coordinated DTE complexes. In this work, the mono- and bimetallic complexes were comparatively studied. The various kinds of ligands on the bimetallic complexes were further explored with the aim to rationalize the relationship between the structure and NLO properties. The closed-ring complexes are named as 1c–5c and the corresponding open forms are 1o–5o in the present paper. We aimed at: (i) elucidating the differences of mono- and bimetallic complexes on the second-order NLO responses; (ii) investigating the effects of various ligands and photoisomerization on geometrical structures, the charge transfer (CT) properties as well as first hyperpolarizabilities.

2. Computational details

All calculations in this paper were carried out by using Gaussian 09W program package [45]. On the basis of experimental data [44], the geometries of 4o complex were optimized in DFT framework by using B3LYP [46,47] and PBE1PBE hybrid functionals [48,49]. The 6-31G(d) all-electron basis set was employed for nonmetal elements, whereas transition metal Pt(II) used SDD basis set with the Stuttgart Dresden effective core potentials. The crystallographic data and calculated geometric parameters of 4o are given in Table S1 (Supporting Information), and the corresponding atom labels are displayed in Fig. S1. The geometric parameters of the all complexes have been optimized by using the PBE1PBE functional, and no symmetry restriction was offered in structure optimization process. Furthermore, frequency calculations were applied to verify that the structures are minima on the energy surface. The bond length alternation (BLA) value is used to measure the degree of delocalization and defined as equation

\[
\text{BLA} = \frac{1}{N} \sum d(\text{single}) - \frac{1}{M} \sum d(\text{double})
\]

Here, M and N indicate the number of double and single bonds along the conjugation path respectively, while d means bond length. With respect to the calculation of the polarizability and hyperpolarizability, one option is to use the derivatives either analytically or numerically. In this paper, the static first hyperpolarizabilities (\( \beta_{tot} \)) were obtained by analytical third energy derivatives owing to more efficient and less expensive. The \( \beta_{tot} \) was calculated by the following equation:

\[
\beta_i = \beta_{ii} + \frac{1}{3} \sum_{j \neq i} (\beta_{ij} + \beta_{ji}) \quad (i, j = x, y, z)
\]
method at the B3LYP/6-31G(d)/SDD level, since the B3LYP functional is in satisfactory agreement with experimental values [44]. The solvent effect has been considered by the polarizable continuum model (PCM) in dichloromethane solvent [58]. To evaluate the charge transfer (CT) abilities process, the CT parameters containing the amount of transferred electrons ($q^{ct}$), the corresponding effective CT distance ($d^{ct}$) and the $t$ index defined as the degree of $\rho^*(r)$ and $\rho^*(r)$ based on the total densities for the ground and excited states are calculated. The larger $t$ index indicates the little overlap between the electron-accepting and electron-donating regions exists.

3. Results and discussion

3.1. Geometrical and electronic structures

Two hybrid functionals B3LYP and PBE1PBE at the 6-31G(d) basis set for nonmetal atoms and SDD basis set for Pt atom were chosen to optimize the geometrical structure of 40 derived from crystal structure. The results illustrate that the geometrical parameter obtained by PBE1PBE functional are in well accordance with the crystal data [44], indicate the geometrical calculations are reliable. Therefore, the geometry structures of open- and closed-ring complexes have been applied at PBE1PBE/6-31G(d)/SDD level. The studied complexes structures are shown in Fig. 1. The optimized calculations display clear differences on two thiophene complexes are higher than those of the corresponding closed-ring complexes. Several pople’s basis set (6-31G(d), 6-31+G(d), 6-31+G(d,p), 6-311+G(d,p)) at the CAM-B3LYP level for 1c complex have been used and listed in Table S3.

3.2. Static first hyperpolarizabilities

As aforementioned, the variations of geometry and electronic structures may inevitably affect the NLO properties. For the sake of confirming the accuracy of $\beta_{tot}$ results, we have adopted three functionals (M06-2X, CAM-B3LYP and ωB97XD) for assessing the effect of DFT functional on the NLO response. The $\beta_{tot}$ values together with the components values obtained by three functionals for studied complexes are listed in Table S2 and plotted in Fig. 2. In all case, the $\beta_{tot}$ values of M06-2X give relatively large values compared to the CAM-B3LYP results, providing a consistent trend for investigating the qualitative second-order NLO properties. In addition, the relational studies show that the CAM-B3LYP functional was proposed as a suitable approach to predict the first hyperpolarizability owing to its semiquantitative accuracy [59]. Hence, we only take the calculated $\beta_{tot}$ values of CAM-B3LYP functional as example to shed light on second-order NLO responses for current systems. Moreover, a suitable basis set is important to calculate the first hyperpolarizability of all studied complexes. Several people’s basis set (6-31G(d), 6-31 + G(d), 6-31 + G(d,p), 6-311+G(d,p)) at the CAM-B3LYP level for 1c complex have been used and listed in Table S3. It is noted that the diffuse functions and polarization have a little influence on the NLO response. Taking the computation costs into account, the $\beta^{tot}$ value of 1c is smaller than that of 1b, whereas the HOMO energy is higher than that of complex 1o. Therefore, it can be seen that the $E_{gap}$ value of 1c is smaller than that of complex 1o by ~1.39 eV. Bear in mind, a lower HOMO–LUMO energy gap would be beneficial to larger NLO response. The HOMO and LUMO energy gaps can be obviously narrowed in closed-ring systems, further predict the $\beta_{tot}$ values may gradually increase.

![Fig. 1. Calculation models of the studied complexes.](image-url)
account, the CAM-B3LYP/6-31 + G(d)/SDD was a proper level to calculate the first hyperpolarizabilities (Table 2). For studied systems, the origin of the cartesian coordinate system is located at the middle of the C–C bond in cyclopentene ring and the horizontal y-axis pointing to phenyl or quinoline moieties.

In the present study, we focused on analyzing the magnitude of first hyperpolarizabilities. As displayed in Table 2, it is clearly seen the computed $\beta_{\text{tot}}$ values of closed-ring increase as the order $\beta_{\text{tot}}$ (3c) $<$ $\beta_{\text{tot}}$ (5c) $<$ $\beta_{\text{tot}}$ (2c) $<$ $\beta_{\text{tot}}$ (4c) $<$ $\beta_{\text{tot}}$ (1c). The results illustrate the same trend in the open-ring complexes. In addition, the closed-ring 1c complex possesses the largest $\beta_{\text{tot}}$ value of 144.86 $\times$ 10$^{-30}$ esu, which is about 3.1 times as large as the 2c. Analogously, the $\beta_{\text{tot}}$ value of 1o complex is maximum value (26.78 $\times$ 10$^{-30}$ esu), almost 2.1 times with respect to 2o. It indicates that bimetallic Pt(II) complexes result a significant decrease of the $\beta_{\text{tot}}$ values of complexes 2c-5c. The plots of $-\gamma_{yy}(r)$ and $-\beta_{yy}(r)$ together with corresponding $\beta_{\text{tot}}$ values of the closed-ring complexes at the CAM-B3LYP/6-31G+(d)/SDD level have been provided in Fig. 3. The local contribution is decomposed into a pair of positive (pink region) and negative (yellow region) parts. It is clearly observed that the region of positive contributions dominate the $-\gamma_{yy}(2)$ and $-\beta_{yy}(2)$ function spreading all over the complexes and prevailing over corresponding negative parts. As a consequence, the components $\beta_{yy}$ and $\beta_{yy}$ represent the large positive values. As visualized in Fig. 3, complex 1c has larger area of positive $\beta$ density, providing a rather large positive $\beta_{yy}$ value (140.4 $\times$ 10$^{-30}$ esu). On the other side, with regard to quinoline-containing complexes 4c and 5c show the area of positive contribution amplitude going much larger than those 2c and 3c. It indicates the off-diagonal $\beta_{yzz}$ values for complexes 4c and 5c would be undoubtedly larger the positive $\beta_{yzz}$ values with respect to 2c and 3c. Therefore, $\beta$-density distributions can be deemed as an efficient auxiliary method to assess the relative magnitudes of the $\beta_{\text{tot}}$ values.

Coming the photoisomerization influence on first hyperpolarizabilities results, the DTE unit undergoes reversible interconversion between a nonconjugated form and $\pi$-conjugated form leading to the large $\beta_{yy}$ total components owing to CT transfer occurring along y-axis. In the case of other pairs of 2–5, a single hyperpolarizability independent tensor component $\beta_{yy}$ is the main contribution for $\beta_{\text{tot}}$. The off-diagonal $\beta_{yzz}$ tensorial component is the dominant one leading to the largest $\beta_{yy}$ total component, indicate the CT transfer occurs on yz-plane. To further explore more intuitive information about the contribution to $\beta$ values, the first hyperpolarizability density analysis which is the spatial electronic contribution to the first hyperpolarizabilities have been performed in this section. The $\beta$ and $\rho_{yy}$ are numerically calculated from the second-order derivative of electron density with respect to an applied electric field and defined according to eq (4)

$$\rho_{yy}(r) = \frac{\partial^2 \rho(r)}{\partial F_y^2}$$

and the $\beta$ values are given by eq (5):

$$\beta_{yy} = \int -\rho_{yy}(r) y \, dr$$

Since the $\beta_{\text{tot}}$ values of open-a and closed-ring complexes are consistent with the same trend, we only focus on the $\beta$ densities of closed-ring complexes. The $\rho_{yy}(r)$ corresponding to $\beta_{yy}$ is the most crucial component of $\beta_{\text{tot}}$ in complex 1c, whereas $\rho_{yy}(r)$ is related to off-diagonal $\beta_{yzz}$ and the main component for complexes 2c-5c. The plots of $-\gamma_{yy}(2)$ and $-\beta_{yy}(2)$ for complexes 2c-5c are much larger than those 2c and 3c. Therefore, $\beta$-density distributions can be deemed as an efficient auxiliary method to assess the relative magnitudes of the $\beta_{\text{tot}}$ values.

### Table 1

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<th>BLA</th>
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</tr>
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<td>2.49</td>
<td>0.066</td>
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</table>

![Fig. 2](image-url)  
**Fig. 2.** Relationship between the $\beta$ (10$^{-30}$ esu) values of the open-ring and the closed-ring complexes computed at various levels of theory.
form 5c

order NLO switching response might be probable candidates for monometallic Pt(II) DTE-based complex with the efficient switching properties on second-order NLO coefficients. It's worth noting the switch ratios of the closed-ring complexes may give rise to relatively high energy absorption at 292 nm along with weak low-energy absorption at 341 nm, which are satisfactory agreement with the experimental data (286 nm and 322 nm) respectively. Hence, a detailed discussion has been performed the crucial transitions in dichloromethane solution with the TD-B3LYP/6-31G(d)/SDD method. To confirm the definition of crucial excited state is credible, we adopted the sum-over-state (SOS) method at the TD-B3LYP level in the framework of SOS perturbation theory. SOS method can preferably provide the contribution to the hyperpolarizabilities from various excited states. In this paper, a total of 100 states were used to adequately acquire the converged \( \beta_{\text{tot}} \) values (Fig. S2). The principal electronic transition parameters corresponding containing absorption wavelengths (\( \lambda \)), oscillator strengths (\( f_{\lambda} \)), the excitation energies (\( \Delta E_{\text{exc}} \)), associated orbital transitions and electron density difference maps (EDDM) of the crucial excited state are compiled in Table S4. The purple color area delegates the electron acceptor, and the blue color region represents the electron donor. The relevant simulation absorption spectra are shown in Fig. S3.

As depicted in EDDM, open-ring complex 1o mainly consists of two absorption bands. Both the S1 (406 nm) and S9 (315 nm) states provide dominant contribution to the \( \beta_{\text{tot}} \) value. The simulated absorption spectrum exhibits one high-energy absorption peak absorbing at 406 nm along with an additional weak low-energy transition absorbing at 315 nm, which are described by the HOMO→LUMO (98%) and HOMO-3→LUMO (93%) excitations, respectively. The electronic transition state S1 absorbing at 406 nm, the HOMO is delocalized through benzene and DTE fragments, whereas the LUMO is located on the metal Pt(II) and pyridine groups. The CT pattern can be designated as intraligand charge transfer (ILCT) transition from benzene ring to pyridine section. Perception of corresponding EDDM reveal that S9 excitation can attribute to a mixed MLCT transitions of Pt(II) atom and pyridine, ILCT from DTE part to pyridine group and a small ligand-to-ligand charge transfer (LL'CT) from the ligand chlorine to pyridine section. As for 1c, the electronic transition state S1 absorbing at 662 nm is formed by the HOMO→LUMO transition, which can be viewed as ILCT transition from the DTE moieties to pyridine ring. According to the EDDM, the S12 electronic transition is categorized as the mixture of LL'CT from ligand chlorine to pyridine, combined with CT trend from benzene to the DTE linker and pyridine moieties and larger MLCT transitions of Pt(II) atom and pyridine. Intriguingly, the difference of \( \beta_{\text{tot}} \) values between open- and closed form is pronounced for all studied complexes. As noted in Fig. S3, remarkable red-shifted from 406 nm to 662 nm are observed in the 1c complex compared with 1o. Moreover, the low-energy absorption bands of closed-ring complexes are bathochromic-shifts with respect to the relevant electronic transitions in the simulated spectra of open-ring complexes. This phenomenon suggests that closed-ring complexes may give rise to relatively high first

<table>
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<tr>
<th>Complexes</th>
<th>( \beta_{\text{tot}} )</th>
<th>( \beta_{\text{tot}} )</th>
<th>( \beta_{\text{tot}} )</th>
<th>( \beta_{\text{tot}} )</th>
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</tr>
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<td>0.7</td>
<td>5.0</td>
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Table 2
The main individual components of first hyperpolarizabilities and total first hyperpolarizabilities (10^{-30} esu) of the studied complexes calculated at CAM-B3LYP/6-31 + G(d)/SDD level.

### 3.3. Absorption spectrum

For the sake of elucidating the origin of the second-order NLO responses for open- and closed-ring complexes, we present herein the UV–vis absorption spectra for these complexes in dichloromethane solution by TD-DFT methodology. To verify the computational results reasonably, various functionals (TD-B3LYP, TD-PBE1PBE, TD-B97X and TD-BHandHLYP) with the same basis set were carried out to simulate the experimental electronic absorption spectra (Fig. 4). It is found that the simulated UV–vis absorption spectrum received from B3LYP contains one intense high-energy absorption at 292 nm along with weak low-energy absorption at 341 nm, which are satisfactory agreement with the experimental data (286 nm and 322 nm) respectively. Hence, a detailed discussion has been performed the crucial transitions in dichloromethane solution with the TD-B3LYP/6-31G(d)/SDD method. To confirm the definition of crucial excited state is credible, we adopted the sum-over-state (SOS) method at the TD-B3LYP level in the framework of SOS perturbation theory. SOS method can preferably provide the contribution to the hyperpolarizabilities from various excited states. In this paper, a total of 100 states were used to adequately acquire the converged \( \beta_{\text{tot}} \) values (Fig. S2). The principal electronic transition parameters corresponding containing absorption wavelengths (\( \lambda \)), oscillator strengths (\( f_{\lambda} \)), the excitation energies (\( \Delta E_{\text{exc}} \)), associated orbital transitions and electron density difference maps (EDDM) of the crucial excited state are compiled in Table S4. The purple color area delegates the electron acceptor, and the blue color region represents the electron donor. The relevant simulation absorption spectra are shown in Fig. S3.

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hyperpolarizabilities values, which is also coincident with the HOMO and LUMO energy gap.

We are interested the influence of various ligands on the second-order NLO properties. The UV–vis spectra of closed-ring complexes 2c-4c are preliminarily analyzed in parallel. As depicted in Table S4, the simulated absorption spectrum of 2c exhibits the electronic transition state S2 absorbing at 475 nm due to HOMO → LUMO+1 (76%) and HOMO-1 → LUMO (22%) transition. The band may be mainly assigned as ILCT [π(DTE) → π*(pyridine)]. The band absorbing at 424 nm is assigned as main contribution ILCT from DTE to pyridine part. Significantly, the mixed CT pattern within the 1c inevitably results in the relatively larger the degree of charge transfer than 2c. Hence, it is confident in attributing the larger βtot value of system 1 than system 2 to their apparent distinct of charge transfer form. Complex 3c has been associated with excited S1 and S5 states one middle-energy electronic transition absorbing at 414 nm and a low-energy electronic transition at 685 nm respectively, and both of the two states can be assigned as ILCT. Note that charge transfer patterns of 3c have been observed quite similar to that of 2c in EDDM. The S1 (673 nm) and S2 (549 nm) states of 4c complex are mainly contributed by the HOMO → LUMO (100%) and HOMO-1 → LUMO+1 (98%) transition respectively, which provide dominant contribution to the βtot value. Both of them can be viewed as ILCT mainly from the middle DTE part to the two quinolone sides. Moreover, 4c obviously enlarge spatial separation of electron density compared with 2c. To sum up, this phenomenon would be conducive to further research that various ligands of metal complexes can affect the degree of charge transfer, which plays a crucial part in the modification of the second-order NLO response.

As is well known, the obvious charge transfer is the indispensable requirement to attain high NLO response. Motivated by this, taking closed-ring complexes as typical, the CT parameters including the magnitude of CT (qCT), the relevant effective CT distance (dCT) and t parameter for the ground state and the excited state are quantitatively evaluated. With a view of visualizing the spatial extent and overlap between the regions of density diminution and increment, the centroids of charge for studied complexes are plotted in Fig. 5. Taking the slight difference on CT patterns of complexes 2c and 3c into consideration, the corresponding parameters are analyzed primarily. The amount of qCT for complex 2c is 0.485 |e|, which is slightly larger than that of 3c (0.469 |e|), and the corresponding dCT value is decreased from 0.404 Å to 0.256 Å. It is obvious that transition of complex 2c present relative stronger CT character than 3c, thus leading to more effective NLO response. Indeed, complexes 2c and 4c show the longer charge transfers length as well as the larger t index assessing the charge separation extent. These quantitative data show that Pt(II) dithienylcyclopentene–based complexes have stronger CT character, accompanied by better second-order NLO properties. It is worth mentioning the closed-ring complex 1c with the larger amount of charge (qCT = 0.493 |e|), the largest associated charge transfer distance (dCT = 2.646 Å) as well as the smaller overlap, suggesting that complex 1c has a maximum CT and obvious spatial charge separation, which is in reasonable agreement with mentioned previous regarding the first hyperpolarizability analysis. Considering the above discussions, it is very meaningful that the quantitative measures of the magnitude and length of the CT process are in favor of the modification of the degree charge transfer. The mononmetallic Pt(II) complexes are predicted to have the superior second-order NLO responses.

3.4. Frequency-dependent first hyperpolarizabilities

It is necessary to decide frequency-dependent properties theoretically result from experimental measurements of βtot values usually include oscillating electric fields. The effect of dispersion behaviors on the second harmonic generation (SHG) β (-2ω; ω, ω) and the electro-optical pockels effect (EOPE) β (-ω; ω, 0) of 1 and 2 systems have been calculated by using coupled perturbed density function theory (CPDFT) method at CAM-B3LYP/6-31 + G*/SDD level. Three optical wavelengths with 1340 nm, 1460 nm and a nonresonant wavelength of 1907 nm were employed to show the dispersion contribution to the NLO response in Table 3. According to the data, it is visualized that the magnitude of β (-ω; ω, ω) and β (-ω; ω, 0) are enhanced with increasing frequency. Moreover, the calculated frequency-dependent β (-2ω; ω, ω) shows the largest frequency dispersion, thus β (-ω; ω, 0) values are larger than those of corresponding static βtot values, which indicates the frequency-
dependent effect on $\beta$ ($-2\omega; \omega, \omega$) are stronger than those of $\beta$ ($-\omega; \omega, 0$) for studied complexes. In addition, the order of $\beta_{\text{SHG}}$ and $\beta_{\text{EPOE}}$ values are identical to that the static $\beta_{\text{tot}}$ values: $1c > 2c > 1o > 2o$. The SHG closed/open $\beta_{\text{ratio}}$ are 14.6 and 8.4, whereas the ratios for EPOE are 6.6 and 4.4 within studied complexes. It is obvious that the dynamic ratios are larger than their static counterparts, the $\beta_{\text{tot}}$ values: $1c$ and $2c$ are nearly the coplanar structure in closed-ring complexes containing perfluorocyclopentene ring decrease the dynamic ratios are larger than their static counterparts, the $\beta_{\text{tot}}$ values.

4. Conclusions

In this paper, the first hyperpolarizabilities of a series of mono- and bimetallic Pt(II) DTE-containing complexes were comparatively studied to rationalize the structure-property relationship. Correlating calculations show the introduction of quinoline into the ligand can substantially raise the spatial charge separation, thus improving the second-order NLO responses. On the contrary, Pt(II) complexes containing perfluorocyclopentene ring decrease the second-order NLO responses. This series of bimetallic Pt(II) model complexes can be altered by various ligands to control their NLO behaviors. Moreover, the TD-B3LYP calculations present the mixed MLCT/ILCT/LLCT transitions within the monometal Pt(II) complexes result in the larger first hyperpolarizabilities values than that bimetallic Pt(II) complexes. More interestingly, we give a number of comments on the switching properties of studied complexes. The photoreponse DTE unit is nearly the coplanar structure in closed-ring complexes along with a better $\pi$-conjugation, which makes a remarkable enhancement of NLO response. The largest $\beta_{\text{tot}}$ contrast (~5.4 times) is found in monometal Pt(II) complexes. The observation is attributed to smaller BLA values and narrowed the energy gap between HOMO and LUMO. We hope this work could be conducive to the perspective for further theoretical and experimental research on rational design for organometalllic DTE-based NLO materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2019.03.009.


