

DFT Studies on Second-order Nonlinear Optical Properties of a Series of Axially Substituted Bis(salicylaldiminato) Zinc(II) Schiff-base Complexes

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Abstract Coordination of an axial ligand to metal center to enhance the second-order nonlinear optical(NLO) response of a two-dimensional bis(salicylaldiminato) zinc(II) Schiff-base complex is an unprecedented model. The second-order NLO responses of a series of axially substituted bis(salicylaldiminato) zinc(II) Schiff-base complexes were explored according to the finite field(FF) method at CAM-B3LYP/6-31+G(*d*) level(LANL2DZ basis set for metal atoms). The results show that the second-order NLO properties can be effectively tuned by exchanging the donor and acceptor of the axial ligand and extending the length of the conjugated bridge along the axial direction. A system involving the electron acceptor along the appropriate direction has a large three-dimensional second-order NLO response. Meanwhile, time dependent density functional theory(TD-DFT) method was employed to calculate the physical parameters of excited states. The results show that the *Y*- and *Z*-polarized transitions of the zinc(II) Schiff-base complex are the first and second excited states, respectively, and have a low-lying excited energy. Although the *X*-polarized transition has a high excited energy, the large oscillator strength indicates that it will significantly contribute to the second-order NLO response.

Keywords Schiff base; Zinc(II) complex; Nonlinear optical property; Axial ligand; Density functional theory

1 Introduction

The design and synthesis of nonlinear optical(NLO) molecular materials have attracted considerable attention due to their unique application in the preparation of optical fibers, data storage, optical limiting, optical computing, optical switching, signal processing, and so on^[1,2]. In the past four decades, considerable efforts have been devoted to this area. A large number of NLO materials have been reported, including inorganic salts^[3], inorganic oxides^[4], metal clusters^[5], quantum dots^[6], organic and organometallic compounds^[7–10], metal complex, and polymer materials^[11,12], and so on. Among them, metal complexes have become important NLO alternative materials because they have a large variety of geometrical structures and diverse electronic properties that can be tuned to optimize their NLO properties, such as extending the π conjugated bridge of organic ligand, changing oxidation state, spin state, and *nd* configuration of metal center^[13–18].

The donor- π -conjugated bridge-acceptor(D- π -A) model, as a simple molecular scheme, has been widely used in the development of second-order NLO molecular materials. Most of the reported metal complexes with good second-order NLO

responses are the 1D systems with D- π -A structure^[19–23]. However, the second-order NLO responses of the macroscopic materials constructed by 1D NLO molecules are far below their microscopic value. This is mainly due to the following two reasons: (I) the 1D NLO molecule with D- π -A structure usually has a large dipole moment, and thus a strong dipole-dipole interaction. It would lead to an antiparallel arrangement of the NLO molecules, which thus makes the macroscopic material have a centrosymmetric structure. The materials with centrosymmetric structure would not have second-order NLO response^[24]. (II) In order to avoid destructive interference of harmonic light, NLO molecules must be arranged in an optimal molecular orientation to meet the phase-matching condition. The phase-matching orientation always leads to low macroscopic NLO responses because the 1D NLO molecule only has one charge transfer axes^[25]. By contrast, the NLO molecule with 2D structure can overcome the problems to some extent. The 2D molecule has two charge transfer axes, and thus a large off-diagonal component. The presence of off-diagonal component ensures a good macroscopic second-order NLO response under phase-matching condition. Moreover, the transition dipole moments of input

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light and output harmonic light are perpendicular to each other because the off-diagonal component leads to the polarization of frequency photons. This indicates that the polarized system will not absorb harmonic light, which thus makes the transparency of material improved effectively. Therefore, the NLO molecules having large off-diagonal tensor components are better than 1D molecules under the phase-matching condition^[26,27].

Schiff-base metal complex is a typical NLO molecular material^[28–35]. The diverse structures of Schiff-base metal complexes provide a very good base for finely tuning their second-order NLO properties. A lot of aniline salicylaldehyde Schiff-base complexes with excellent second-order NLO properties have been reported by Di Bella *et al.*^[36–41]. Their work almost focused on the 2D planar bis-Schiff-base metal complexes. Recently, a bis(salicylaldiminato) zinc(II) Schiff-base complex has been reported by Di Bella's group^[42]. This complex formed a monomeric adduct[an axially substituted bis(salicylaldiminato) zinc(II) Schiff-base complex], where a Lewis base ligand(pyridine) axially coordinated to the zinc(II) center. This adduct possesses a very high NLO response due to the introduction of the axial ligand according to the electric field induced second harmonic generation(EFISHG) measurement. This represents an unprecedented model for improving the second-order NLO response of metal complex, which is thus worthy to be explored further.

In the present work, second-order NLO properties of a series of axially substituted bis(salicylaldiminato) zinc(II) Schiff-base complexes were studied *via* density functional theory(DFT) calculation combined with finite field(FF) method. The relationship between multidimensional second-order NLO response and the nature of axial ligand was discussed detailedly.

2 Computational Details

All the molecular geometries were optimized *via* DFT method at the B3LYP^[43]/6-31G(*d*) level(LANL2DZ basis set for metal atoms), and then the frequency was calculated at the same theoretical level. No imaginary frequencies were obtained, conforming that the optimized structures reside at minimal point of their potential energy surface.

The FF method has been widely used to calculate second-order NLO responses of molecules^[44–46]. In a static electric field, the energy E of molecule can be unfolded by Taylor series^[47].

$$E = E^{(0)} - \mu_i F_i - \alpha_{ij} F_i F_j - \beta_{ijk} F_i F_j F_k - \gamma_{ijkl} F_i F_j F_k F_l - \dots \quad (1)$$

where all the subscripts correspond the x, y, z of the Cartesian coordinates, $E^{(0)}$ is the energy of molecule without external field, F_i is the component of i -direction in the external electric field, μ_i is the molecular dipole moment vector, α is the linear polarizability tensor, β and γ are the first and second hyperpolarizability tensor, respectively. In Gaussian 09 program^[48], the numerical FF procedure is adopted to calculate the first hyperpolarizability. The field dependence of the energy was generated from the Gaussian 09/SCI calculation in this work. It is clear that the numerical accuracy of the FF equation is associated with the precision in the field dependence of energy

calculations. In order to reduce the error from the energy calculations, an appropriate choice of field amplitude is important. In the present work, a field amplitude of 0.0010 a.u., which has been demonstrated to be effective for the calculation of the static first hyperpolarizability in many literatures, was chosen to calculate the first hyperpolarizability. To improve the accuracy of the calculated first hyperpolarizability, the high-order hyperpolarizability contaminations have to be removed with the aid of the iterative Romberg formula in Gaussian 09 program.

In this paper, the static first hyperpolarizability tensor of molecule was calculated with DFT-FF method at CAM-B3LYP/6-31+G(*d*) level(LANL2DZ basis set for metal atoms). It should be emphasized that the conventionally generalized gradient approximation and localized density approximation of DFT method cannot obtain reasonable results in the calculation of the first hyperpolarizability. To overcome this problem, an exchange-correlation functional with good long-range correction behavior was developed. It has been reported that long-range corrected functional CAM-B3LYP can better estimate the first hyperpolarizability of molecules with D- π -A structure^[49]. In this paper, the first hyperpolarizability was calculated *via* CAM-B3LYP functional. The first hyperpolarizability tensor, β_{tot} , was calculated with the following equation:

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (2)$$

where $\beta_x, \beta_y, \beta_z$ were obtained by

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

The polarizability α_s was obtained with the following formula:

$$\alpha_s = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) / 3 \quad (4)$$

In order to get an insight into the second-order NLO response, the excited-state physical parameters of a series of zinc Schiff-based complexes were also calculated *via* TD-DFT method. It has been proved that TD-DFT is a usefully accurate approach for the calculation of low-lying single excitations^[50–52]. The TD-DFT method was used to calculate the electronic absorption spectrum of all the metal complexes at B3LYP/6-31+G(*d*) level(LANL2DZ basis set for metal atoms) in this work. All the calculations were performed *via* the Gaussian 09 program package^[48].

3 Results and Discussion

3.1 Molecular Geometries and Second-order NLO Properties

A typical aniline salicylaldehyde zinc(II) Schiff-base metal complex end-capped with an electron donor and acceptor was defined as the reference molecule(RM) in this work. And a series of 3D axially substituted bis(salicylaldiminato) zinc(II) Schiff-base complexes have been designed by introduction of an axial ligand(pyridine) and electron donor and acceptor based on RM. As shown in Fig.1, the exchange of donor and acceptor has been denoted as A and A', where A=1, 2, 3, and 4. For the 2D RM, it has an A- π -D- π -A structure, and possesses two charge transfer axes. The angle between the two charge transfer axes is defined as θ (see Fig.1). The calculated θ values of all

the metal complexes are listed in Table 1. It can be found that the θ value is almost independent of the axial ligand. The calculated θ value is in a small range of from 61° to 62° .

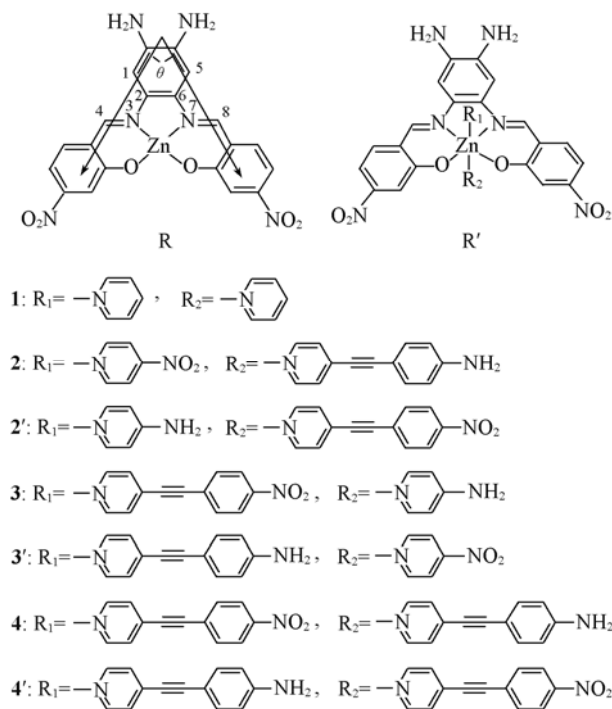


Fig.1 Structures of Schiff-base complexes

Table 1 Angles, θ , between two charge transfer axes and two dihedral angles of metal complexes obtained by B3LYP/6-31G(*d*) calculations (LANL2DZ basis set for metal atoms)

| Complex | $\theta(^{\circ})$ | $\angle C1C2N3C4(^{\circ})$ | $\angle C5C6N7C8(^{\circ})$ |
|---------|--------------------|-----------------------------|-----------------------------|
| RM | 61.25° | -15.69° | 10.54° |
| 1 | 61.92° | -25.11° | 23.48° |
| 2 | 62.12° | -24.69° | 23.17° |
| 2' | 62.06° | -25.31° | 23.63° |
| 3 | 61.96° | -25.49° | 23.78° |
| 3' | 62.00° | -24.74° | 22.73° |
| 4 | 62.15° | -24.94° | 23.09° |
| 4' | 61.87° | -25.16° | 22.94° |

The geometry optimization shows that the aniline salicylaldehyde zinc(II) Schiff-base segment is non-planar due to the introduction of a series of axial ligands in the series 3D systems. The two dihedral angles ($\angle C1C2N3C4$ and $\angle C5C6N7C8$, see Fig.1), which clearly describe their geometries, are also shown in Table 1. The result shows that both the dihedral angles get a significant change relative to RM as the introduction of axial ligands. The dihedral angle $\angle C1C2N3C4$ decreases from -15.69° to -25.11° , and the dihedral angle $\angle C5C6N7C8$ increases from 10.54° to 23.48° (RM vs. complex 1). Although the two dihedral angles are also affected by other factors in axially substituted species (complexes 1–4'), the variation of them is not significant (see Table 1).

The polarizabilities of all the metal complexes were calculated at CAM-B3LYP/6-31+G(*d*) level (LANL2DZ basis set for metal atoms) in this work. The calculated polarizability components (α_{xx} , α_{yy} and α_{zz}) and their average values α_s are

listed in Table 2. It can be found that the introduction of axial ligand enhances the polarizability of all the axially substituted bis(salicylaldehyde) zinc(II) Schiff-base complexes relative to that of RM. Complex 4' possesses the largest polarizability among them. The calculated α_s value is *ca.* twice as large as that of RM. Since the RM is fixed into the *YZ* plane, the α_{yy} and α_{zz} components significantly contribute to the value of α_s . The *X*-axis is the axial direction. And thus a significant enhancement of α_{xx} component can be found as the introduction of the axial ligand. We have also noted that the other two components α_{yy} and α_{zz} are affected by the axial ligand. Especially for systems 4 and 4', their axial ligands possess the longest π -conjugated chain among all the metal complexes studied here. The three components α_{xx} , α_{yy} and α_{zz} of both the systems are larger than that of others according to our DFT calculations. This result indicates that lengthening the π -conjugated chain along axial direction effectively increases not only the α_{xx} value but also the α_{yy} and α_{zz} values. For the system with the same π -conjugated chain of axial ligand, exchanging the positions of electron donor and acceptor along axial direction cannot largely affect their polarizabilities (complex 2 vs. complex 2', complex 3 vs. complex 3', and complex 4 vs. complex 4').

Table 2 Polarizabilities (α_s) of all the metal complexes obtained by CAM-B3LYP/6-31+G(*d*) calculations (LANL2DZ basis set for metal atoms)

| Complex | $\alpha_{xx}/\text{a.u.}$ | $\alpha_{yy}/\text{a.u.}$ | $\alpha_{zz}/\text{a.u.}$ | $\alpha_s/\text{a.u.}$ |
|---------|---------------------------|---------------------------|---------------------------|------------------------|
| RM | 156.282 | 539.124 | 520.620 | 405.342 |
| 1 | 600.804 | 351.666 | 582.696 | 511.722 |
| 2 | 746.843 | 661.760 | 620.571 | 676.391 |
| 2' | 742.199 | 649.739 | 624.252 | 672.063 |
| 3 | 705.681 | 695.450 | 622.675 | 674.602 |
| 3' | 711.683 | 685.287 | 638.043 | 678.338 |
| 4 | 1002.808 | 736.449 | 694.401 | 810.886 |
| 4' | 1012.507 | 721.395 | 697.919 | 810.607 |

The first static hyperpolarizabilities of all the metal complexes were calculated *via* DFT-FF method at CAM-B3LYP/6-31+G(*d*) level (LANL2DZ basis set for zinc atoms) in this work. The calculated β values are listed in Table 3. The result shows that the second-order NLO properties of these metal complexes are sensitive to the nature of axial ligand. The calculated β_{tot} value decreases in the following order: complex 4' > complex 3' > complex 4 > complex 2' > RM > complex 2 > complex 3. A *ca.* twice-fold enhancement of the β_{tot} value has been obtained as the introduction of the axial ligand (complex 4' vs. RM). A detail comparison of the calculated β_{tot} values shows that exchanging the positions of the donor and acceptor of axial ligands would affect the β_{tot} value (complex 3 vs. complex 3' and complex 4 vs. complex 4'). The β_{tot} value of complex 3' is *ca.* 1.95 times as large as that of complex 3. For complexes 3 and 3', they have the same π -conjugated chain in their axial ligands. The difference between them is from the positions of electron donor and acceptor. As mentioned above, the aniline salicylaldehyde zinc(II) Schiff-base segment is non-planar and may be viewed as a curved surface. Our DFT-FF calculation shows that the introduction of an electron acceptor along the direction of curve radius (complexes 3' and 4') would be beneficial to enhancing the second-order NLO responses. We have

Table 3 Second-order NLO coefficients β (a.u.) of all the metal complexes obtained by CAM-B3LYP/6-31+G(d) calculations(LANL2DZ basis set for metal atoms)

| Complex | β_{xxz} | β_{yyz} | β_{zzz} | $\beta_{yyz}/\beta_{zzz}(u)$ | $\beta_{xxz}/\beta_{yyz}/\beta_{zzz}$ | β_{tot} |
|-----------|---------------|---------------|---------------|------------------------------|---------------------------------------|---------------|
| RM | — | -4072.01 | -3349.40 | 1.22 | — | 7320.01 |
| 2 | -7565.47 | -2782.53 | -1787.37 | 1.56 | 4.23:1.56:1 | 7048.56 |
| 2' | 3101.88 | -2735.15 | -1670.91 | 1.66 | -1.86:1.64:1 | 7912.05 |
| 3 | -2322.65 | -3162.51 | -2637.94 | 1.20 | 0.88:1.20:1 | 5948.22 |
| 3' | 8414.21 | -3189.05 | -2627.52 | 1.21 | -3.20:1.21:1 | 11575.09 |
| 4 | 561.71 | -3032.43 | -2409.97 | 1.26 | -0.23:1.26:1 | 8542.42 |
| 4' | 10328.48 | -2986.88 | -2176.10 | 1.37 | -4.75:1.37:1 | 13755.05 |

also noted that the β_{tot} value increases as lengthening the conjugation chain of the axial ligand(complex **2'** vs. complex **4'**).

For the reference molecule(RM), it has a 2D second-order NLO properties. The in-plane nonlinear anisotropy concept(u), which depends on the ratio of $u=\beta_{yyz}/\beta_{zzz}$ ^[26], has been introduced to display the 2D second-order NLO properties of these metal complexes. The calculated u values are listed in Table 3. The result shows that all the metal complexes studied here possess a large in-plane nonlinear anisotropy, and the calculated u values range from 1.2 to 1.7. This indicates that all the metal complexes have a large off-diagonal element β_{yyz} relative to their diagonal element β_{zzz} . Introduction of the axial ligand does not largely affect the magnitude of off-diagonal element β_{yyz} compared with that of RM. We knew very well that the in-plane nonlinear anisotropy of 2D molecule is closely associated with the θ angle between the two charge transfer axes. As mentioned above, the variation of calculated θ value is not substantial with the introduction of the axial ligand. This result is in good agreement with the DFT-FF calculation of the in-plane nonlinear anisotropy.

For the axially substituted complexes **2—4'**, they have 3D second-order NLO properties. Three tensor components, β_{xxz} , β_{yyz} , and β_{zzz} have become important in these 3D systems. Obviously, the large contribution of the new off-diagonal tensor β_{xxz} relative to that of the 2D molecule RM mainly arises from the introduction of axial ligand along the X direction. As shown in Table 3, the ratio of three tensor components($\beta_{xxz}/\beta_{yyz}/\beta_{zzz}$) is closely associated with the positions of the electron donor and acceptor(complex **2** vs. complex **2'**, complex **3** vs. complex **3'**, and complex **4** vs. complex **4'**). Especially for complexes **3'** and **4'**, the electron acceptor was assigned to the direction of curve radius, the off-diagonal tensor β_{xxz} is the dominant component among all the β tensors. Although the ratio of three tensor components is also related to the length of conjugated chain,

the change of the ratio is not substantial upon lengthening the conjugation chain of the axial ligand compared with the exchanging positions of the electron donor and acceptor.

3.2 TD-DFT Studies

On the basis of the large second-order NLO response of complex **4'**, the excited-state physical parameters of this system and the reference system RM were calculated *via* TD-DFT method at B3LYP/6-31+G(d) level(LANL2DZ basis set for metal atoms) in this work. The calculated excited energy(ΔE_{ge}), oscillator strength(f), transition dipole moment(μ_{ge}^i), and major contributions of these low-lying excited states are listed in Table 4. For the 2D system RM, the transition dipole moment element μ_{ge}^Y is the dominant component in the first excited state. This indicates that the first excited state is associated with the Y -polarized transition. And the transition dipole moment element μ_{ge}^Z is the dominant component in the second excited state. This indicates that the second excited state is related to the Z -polarized transition. The Z -polarized transition contributes to the diagonal tensor β_{zzz} , and Y -polarized transition accounts for the off-diagonal tensor β_{yyz} . It is well known that the first hyperpolarizability is proportional to the oscillator strength and inversely proportional to the cube of excited energy of the low-lying charge transfer excited state. As shown in Table 4, the magnitude of excited energy and oscillator strength of both the excited states are on the same order(the excited state 1 vs. 2), it indicates that the diagonal and off-diagonal tensors should be on the same order, which is in good agreement with the DFT-FF calculation($u=\beta_{yyz}/\beta_{zzz}=1.22$, see Table 3).

The first and second excited states of 3D complex **4'** are respectively related to the Y - and Z -polarized transitions according to their transition dipole moment elements, which is similar to that of the 2D RM. This indicates that the

Table 4 TD-DFT results of RM and complex **4'** obtained by B3LYP/6-31+G(d) (LANL2DZ basis set on metal ion)

| Complex | Excited state | f | $\Delta E_{ge}/\text{eV}$ | μ_{ge}^X | μ_{ge}^Y | μ_{ge}^Z | Major contribution |
|---------|---------------|------|---------------------------|--------------|--------------|--------------|--|
| RM | 1 | 0.30 | 2.87 | 0.00 | 2.07 | -0.03 | HOMO \rightarrow LUMO(71%) HOMO-1 \rightarrow LUMO+1(18%) |
| | 2 | 0.57 | 3.20 | -0.12 | 0.00 | -2.69 | HOMO-1 \rightarrow LUMO(43%) HOMO \rightarrow LUMO+1(41%) |
| | 4' | 1 | 0.20 | 2.79 | 0.01 | 1.72 | -0.01 |
| | 2 | 0.40 | 3.05 | -0.62 | 0.00 | 2.24 | HOMO \rightarrow LUMO+2(48%) HOMO-1 \rightarrow LUMO+1(39%) |
| | 10 | 1.69 | 3.96 | 4.17 | -0.01 | 0.33 | HOMO-2 \rightarrow LUMO+3(64%) |

introduction of axial ligand does not largely affect the nature of polarized transition of the first and second excited states for 3D complex **4'**. Owing to the axial ligand along the *X*-direction, the excited state 10 for 3D complex **4'** is associated with the *X*-polarized transition. Although the excited energy of the *X*-polarized transition is larger than those of the *Y*- and *Z*-polarized transitions, the oscillator strength of the *X*-polarized transition is the largest. The large oscillator strength of the *X*-polarized transition indicates that it will also significantly contribute to the second-order NLO response, and thus a large off-diagonal tensor β_{xxz} . All the results support the DFT-FF calculations for the ratio of three tensor components ($\beta_{xxz}/\beta_{yyz}/\beta_{zzz}=-4.75:1.37:1$).

The question we are now concerned with is the nature of the orbital transition of 3D complex **4'**. As shown in Table 4, the first excited state (*Y*-polarized transition) is formed by the HOMO \rightarrow LUMO+1 (69%) and HOMO-1 \rightarrow LUMO+2 (20%) transitions according to our TD-DFT calculations. The second excited state (*Z*-polarized transition) arises from the HOMO \rightarrow LUMO+2 (48%) and HOMO-1 \rightarrow LUMO+1 (39%) transitions. The excited state 10 (*X*-polarized transition) mainly consists of HOMO-2 \rightarrow LUMO+3 (64%) transition. These frontier molecular orbitals of 3D complex **4'** are shown in Fig.2. For the first and second excited states, it can be found that the HOMO and HOMO-1 are mainly localized on the electron donor, the benzene ring of the Schiff base fragment in *YZ* plane. And the LUMO+1 and LUMO+2 are mainly localized on the electron acceptor and benzene ring of the Schiff base fragment in *YZ* plane, which indicates that the excitation corresponding to these orbital transition would give a charge transfer from electron donor to the acceptor end in *YZ* plane, and would contribute to the β_{yyz} and β_{zzz} components. By contrast, the HOMO-2 is delocalized over the electron donor end along the *X*-direction, and LUMO+3 is also delocalized over the electron donor end along the *X*-direction, which indicates that the excited state 10 of 3D complex **4'** can be viewed as a very weak CT transition at the donor end and would contribute to the off-diagonal tensor β_{xxz} component. This indicates that the acceptor unit does not display the electron acceptor character in this 3D system.

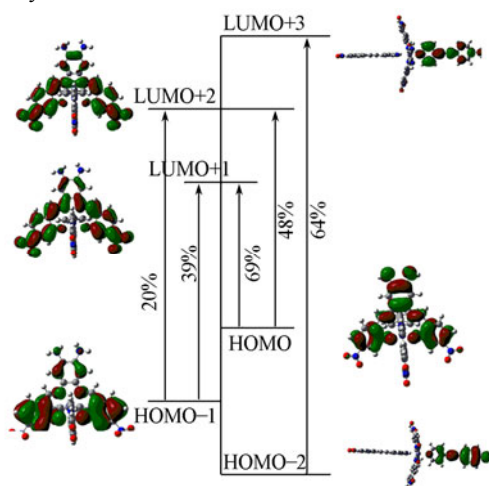


Fig.2 Frontier molecular orbitals related to excitations of complex **4'**

4 Conclusions

Introduction of an axial ligand into a 2D Schiff base Zn(II) complex to enhance its second-order NLO response as an unprecedented model has been explored based on DFT-FF calculations at CAM-B3LYP/6-31+G(*d*) levels (LANL2DZ basis sets on metal atom) in this work. The results show that the second-order NLO properties of these complexes can be optimized by exchanging donor and acceptor and extending the length of the conjugated chain along the axial direction. Our DFT-FF calculations show that the ratio of the three tensor components ($\beta_{xxz}/\beta_{yyz}/\beta_{zzz}$) is associated with the positions of the electron donor and acceptor. Complex **4'** involving the electron acceptor along the appropriate direction has the largest 3D second-order NLO response among all our studied systems. TD-DFT calculations show that the first and second excited states of the zinc(II) Schiff-base complex are related to the *Y*- and *Z*-polarized transitions. Although the *X*-polarized transition has a high excited energy compared to the *Y*- and *Z*-polarized transitions, the large oscillator strength indicates that it will significantly contribute to the second-order NLO response. Meanwhile, the nature of the orbital transition has also been analyzed according to TD-DFT calculations. All the results in the present paper indicate that these metal complexes possess excellent 3D second-order NLO responses.

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