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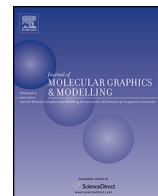
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Theoretical study on photophysical properties of Pt(II) triarylborons with a 2,2'-bpy core derivatives

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ABSTRACT

The photophysical properties of the linear and v shaped Pt(II) triarylborons with a 2,2'-bpy core derivatives have been investigated by density functional theory (DFT) method. The calculated electronic absorption wavelengths are in agreement with experimental ones, which can be described as a mixed transition of intra-ligand charge transfer (ILCT), ligand to ligand charge-transfer (LLCT), and metal-to-ligand charge transfer (MLCT). It is found that the MLCT transition is mainly responsible for the low-energy absorption band with relative smaller oscillator strength, while the high-energy absorption band mainly derives from ILCT and LLCT transition. Moreover, the electron absorption wavelengths are not only dependent on the position of the Ph-BMes₂ but also on the electron-accepting ability of the acceptor groups. The first hyperpolarizability values of the v shaped complexes are larger than that of the linear shape complex, which indicates that larger intramolecular charge transfer for the v shaped complexes will come into being under the external electric field. Moreover, these complexes exhibit two-dimensional second-order nonlinear optical (NLO) character. Thus, the studied complexes have a possibility to be excellent second-order NLO materials. Based on the two-level model, the variation of first hyperpolarizabilities of the studied complexes can be explained by the combined effect of the difference between the ground state and excited state dipole moment, the oscillator strength, and the cube of the transition energy.

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1. Introduction

Transition metal complexes are of great significance owing to their uniquely physical/chemical properties in catalytic application [1], petroleum industry [2], diverse bioorganic and synthetic chemistry [3], nonlinear optics [4], and luminescence [5]. Therefore, there has been an increasing interest in this field and enormous progress has been made in recent times.

Second-order nonlinear optical (NLO) materials have been extensively exploited in both theory and experiment as their diverse applications in optoelectronic and photonic such as electronic-optical devices, advanced telecommunications, and all-optical data processing technologies [6–13]. The most common NLO compounds are donor– π –acceptor (D– π –A) structure in which the intra-molecular charge transfer (ICT) may be occurring. However, some problems have been found in these traditional compounds such as the trade-off between the transparency and macroscopic NLO responses, that is the increase in first

hyperpolarizability (β) is always accompanied by a bathochromic shift of the absorption spectra [14]. Another problem is the centrosymmetric arrangement in crystal as the dipole–dipole intermolecular interaction leads to macroscopically NLO response disappearing [15]. Nowadays, much attention has been paid to transition metal complexes in relation to the metal *nd* configuration, oxidation state, spin state, etc. [16,17]. Comparing with traditional dipolar chromophores, the transition metal plays three important roles in NLO activity [18]: (i) a powerful template to gather ligands in predetermined octupolar arrangements; (ii) a low-energy metal–ligand charge transfer transition (MLCT); and (iii) a Lewis acid to induce a strong intra-ligand charge transfer (ILCT) transition. For example, the transition metal complexes Ru(II) [19], Fe(II) [20], Pt [21], Cr [22], and Ni [23] have shown various second-order NLO properties. Moreover, the transition metal complexes combining with porphyrine, pyridine and bipyridine and/or carborane have appeared as important alternatives for the designing of NLO materials [24,25]. Now, the transition metal complexes have offered a large variety of bulk structures and can satisfy different aspects of second-order NLO materials [26–29].

In addition, three-coordinate organ boron complexes have attracted an increasing attention for their broad applications in organic light-emitting diodes (OLED) [30], nonlinear optics [31],

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and small-molecule activation [32]. Due to the vacant *p*-orbital on the boron atom, the three-coordinate organ boron complexes may exhibit interesting nonlinear optical properties when accompanied with the electron donors. Although the three-coordinate boranes are normally unstable toward hydrolysis, a large degree of stability can be conferred on these compounds through the use of bulky substituent on the boron atom, such as the 2,4,6-trimethylphenyl which protect the vacant *p*-orbital from attack by external nucleophiles [33]. Such compounds have also been examined by cyclic voltammetry, which indicates that the dimesitylboryl (BMes₂) group is considered to be an electron acceptor comparable in strength to the CN group [34,35]. Using the BMes₂ group as an electron acceptor, the donor–acceptor compounds might exhibit excellent nonlinear optical response. Additionally, the Mes group of BMes₂ can be replaced by the C₆F₅ of the pentafluorophenyl copper [36] and the transition metal can also be incorporated with coordinated boron [37], which formed a large and varied family of generally stable, highly robust system. These complexes offer a number of potentially advantages in the development of new electronic, magnetic, and optical materials [38].

Recently, four 2,2'-bipyridine-based complexes functionalized by either B(Mes)₂-phenyl or Nphenyl-5,5'-(*p*-BMes₂-phenyl)₂-2,2'-bpy (Pt (5,5'-BP2bpy) Ph₂, **1a**), 4,4'-(*p*-BMes₂-phenyl)₂-2,2'-bpy (Pt (4,4'-BP2bpy) Ph₂, **2a**), 4-(*p*-BMes₂-phenyl)-4'-(*p*-NPh₂-phenyl)-2,2'-bpy (Pt (4,4'-BPNPbpy) Ph₂, **3a**), and 4,4'-(*p*-NPh₂-phenyl)₂-2,2'-bpy (Pt (4,4'-NP2bpy)Ph₂, **4a**) have been synthesized and fully examined by electrochemical, absorption, and luminescence spectroscopic analysis [39]. As the lone pair of electrons in the N atom, the NPh₂ is an electron donor group. Thus, the studied complexes have different electron donor groups (**4a**), electron acceptor groups (**1a** and **2a**) or their combination (**3a**). We hope that these complexes might provide new opportunities for second-order NLO materials.

2. Computational details

In the present work, all the calculations were carried out using the Gaussian 09W program package [40]. The geometrical optimization of the studied complexes without any symmetry constraint was carried out using the Becke's three-parameter exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP) of density functional theory (DFT). Taking into account the relativistic effect for transition-metal ion, the effective core potential (ECP) double- ζ (DZ) basis set of LanL2DZ is applied for the Pt atom and the 6-31G* basis set is used for the nonmetal atoms. Harmonic vibrational frequency calculations were used to confirm that the optimized structures were minima, as characterized by positive vibrational frequencies. The time dependent (TD) PBE1PBE which contains 25% exchange and 75% correlation weighting, also known as PBE0, is employed to simulate the absorption spectra of the studied complexes. This method is obtained by casting a pure functional of Perdew, Burke and Ernzerhof [41,42] into hybrid by Adamo [43]. It was shown that this method can improve the accuracy of excitation energies and charge transfer bands in metal complexes for both gas phase and solution calculations [43–45]. Also, the solvent effects on the electron excitations were considered and the polarizable continuum model (PCM) [46] was employed in the TDDFT calculations for some selected complexes. For the first hyperpolarizability, a new functional, the coulomb-attenuated hybrid exchange-correlation functional (CAM-B3LYP) has been shown to properly predict the first hyperpolarizability of the charge-transfer process and given a reliable results for the metallic organ boron molecules [28,45,25]. Moreover, it is reported that the mPWPW91* is also an excellent hybrid functional in predicting the NLO property for the transition metal complex [47]. In

our previous paper, we have shown that the two functionals show the same trend in the calculation of NLO property for the Pt(II) bpy derivatives [45]. In the present work, the CAM-B3LYP/6-31+G* was employed to calculate the first hyperpolarizability of all the complexes and the LanL2DZ was applied for the Pt atom.

It is demonstrated that the finite field (FF) approach can broadly be applied to calculate the first hyperpolarizability. When a weak and stable electric field (*F*) is added, the energy of the molecule is shown as

$$E = E^{(0)} - \mu_i F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l - \dots \quad (1)$$

where $E^{(0)}$ is the molecular energy in the absence of the applied electric field, and the *i*, *j*, *k*, and *l* represent different components *x*, *y*, or *z*, μ is the molecular dipole permanent moment, where α , β and γ are the polarizability, first, and second hyperpolarizability tensors, respectively. In this paper, we calculated the first hyperpolarizability β_{tot} with the formula defined as:

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

where

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

3. Results and discussion

3.1. Geometrical configuration analysis

For the transition metal Pt, the electronic configuration is d^8 , and the geometry is square planar [48]. Thus, there are two possible spin states, the closed-shell singlet and open-shell triplet. For the Pt(BNbp)₂Ph₂ [45], the closed-shell singlet is more stable than that of the open-shell triplet. Therefore, closed-shell singlet of the studied complexes was used in the present work. The geometric structures of the studied complexes (Fig. 1) with all real frequency have been obtained at the B3LYP/6-31G* level (LanL2DZ basis set on the metal ion). The calculated energy gaps for the complexes are consistent with that experimentally observed ones (Table S1). For the linear complex **1a** and v shaped complex **2a**, the total energy of v shaped **2a** is about 0.2 kcal/mol lower than that of the linear **1a**, which means that **2a** is slightly more stable than **1a**.

The selected bond distances of the optimized complexes were shown in Table S2. Most of the bonds change slightly on moving the 5,5'-position to the 4,4'-position for the Ph-BMes₂ group. Comparing with the linear complex (**1a**), the increasing bond lengths are the C3–C4, C3–C5, C5–C7, C6–C8, C11–N1 and C12–N2 within 0.006–0.016 Å; the bond lengths of C3–C5, C4–C6, C9–C11, C10–C12, Pt–N1, and Pt–N2 decrease within 0.003–0.015 Å for these v shaped complexes **2a–4a** (number of atoms, see Fig. S1). Meanwhile, the length of C7–C9, C15–N17, N17–C19, N17–C21 and the corresponding of the right branch decrease.

3.2. Absorption spectra and electronic transition properties

TDDFT method has emerged as a powerful tool for the investigation of electronic transition properties [49–52]. In Table 1, we summarized the absorption energies, oscillator strength, and major transition nature for the studied complexes at the TDPBE1PBE/6-31+G* level of theory, as compared to experimental data. The calculated absorption wavelengths are in agreement with the experimental ones, confirming the suitability of selected method for this type of calculations. According to earlier reports, the solvent effects have a critical influence on the electronic absorption spectra [53,54]. To account for the effect of the dichloromethane (CH₂Cl₂) solvent, the above calculation for complex **1a** was repeated under

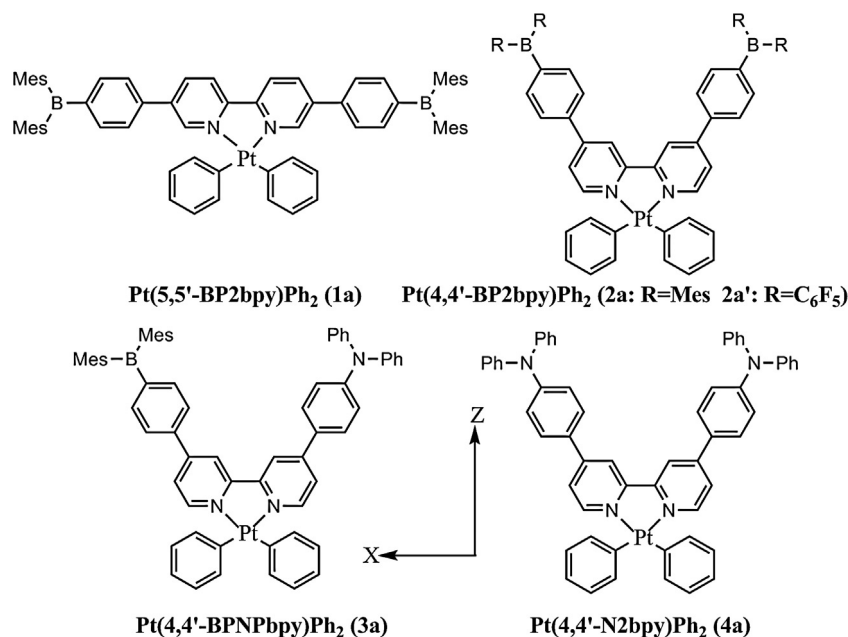


Fig. 1. The chemical structures and the axes convention used in theoretical calculations.

PCM conditions. The difference between the gas and solvent phase is within 6 nm (Table S3), which indicates the solvent effect does not improve the agreement between measured and calculated electron absorption spectra. Thus, the results derived from the gas phase calculation were used in the following discussion.

Although the studied complexes exhibit an intense absorption band and a weak absorption band, these band positions are strongly dependent on the molecular structures and substituents. The complex **1a** was taken as an example to analyze the electron transition property (Fig. 2). For the intense absorption band at about 380 nm, the three concerned occupied orbitals are mainly localized on the *p* orbital of B atom and π orbital of the Mes, while the unoccupied orbitals are primarily π^* orbitals on the bpy moiety, which can be assigned as a mixed transition ILCT and LLCT. For the weak absorption band at about 517 nm, the occupied orbitals are mainly localized on the *d* orbital of Pt, while the unoccupied orbitals are the π^* orbital of the bpy, which was assigned as MLCT transition. It means that transition property influences the relative intensity of absorptions peaks. The obvious intramolecular charge transfer may be helpful for the first hyperpolarizability. Moreover, the absorption energy of the linear complex **1a** is lower than that of the v shaped complexes such as **2a**, indicating that the impact of the BMe₂ as an electron-accepting group decreases as its location from the 5,5' to 4,4'-substitution.

Among the v shaped bpy complexes, their electron transition properties are similar with those of **1a**. The intense absorption bands also mainly derive from the mixed transition of ILCT and

LLCT, and the weak absorption bands are mainly result from MLCT (Fig. 3). Moreover, the MLCT energy follows the order: **4a** (479 nm) < **3a** (500 nm) < **2a** (508 nm), which is in agreement with the electron-accepting nature of the boron center [39]. Specially, the two absorption bands of **2a'** are located at 418 nm and 579 nm (Table 1), which are much lower than the others. It means that the electron-accepting ability of the B(C₆F₅)₂ is significantly stronger than that of B(Mes)₂ group.

To further study the electronic transition property, the total density of states (TDOS) and the partial density of states (PDOS) calculations were carried out by Aomix program for the low-energy transition. As shown in Fig. 4, the Pt(II) atom plays a significant role in the formation of the occupied molecular orbitals (such as HOMO-2) for all the complexes, while the B atoms mainly contribute to the unoccupied molecular orbitals (such as LUMO). Besides the Pt(II) atom, the N atoms of NPh₂ also make a contribution to the occupied molecular orbital (HOMO-2) of **3a** and **4a**. In summary, Pt (II) and N atoms mainly exhibit electron donor character, and the B atom plays a role in withdrawing electron. In addition, the contribution of different atoms to the low-energy transition orbitals has been listed in Table S4. For all the complexes, the main contribution comes from the Pt(II) atom reaching to twenty percent and the contribution of B atom almost zero in relation to HOMO-2 orbital. While for the LUMO orbital, the contribution of Pt(II) significantly reduces to 2–5 percent and the B atom reaches to about ten percent. It is noted that the changes are obvious for the **2a'** such as the Pt (II) makes almost eighty percent (77.22%) contribution to the HOMO-2 orbital

Table 1

The experiment and calculated absorption data and the transition nature of studied complexes by TD-PBE1PBE/6-31+G* method.

Complex	$\lambda_{\text{max,exp}}$	$\lambda_{\text{max,cal,gas}}$	f_{os}	Transition nature
1a	369	380	0.948 (S14)	H-8 \rightarrow L (58%) H-6 \rightarrow L (17%) H-15 \rightarrow L (17%)
	468	517	0.033 (S3)	H-2 \rightarrow L (70%)
2a	330	368	0.346 (S14)	H-3 \rightarrow L+1 (55%) H-6 \rightarrow L (29%) H-5 \rightarrow L+1 (24%)
	460	508	0.129 (S3)	H-2 \rightarrow L (66%) H \rightarrow L+1 (17%) H-2 \rightarrow L+2 (13%)
2a'		418	0.201 (S16)	H-6 \rightarrow L (65%) H-5 \rightarrow L+1 (18%) H-6 \rightarrow L+2 (16%)
		598	0.099 (S4)	H-2 \rightarrow L (63%) H-1 \rightarrow L+1 (25%) H-2 \rightarrow L-2 (13%)
3a	345	363	0.201 (S17)	H-4 \rightarrow L+1 (43%) H-9 \rightarrow L (25%) H-6 \rightarrow L+1 (23%)
	418	500	0.169 (S3)	H-2 \rightarrow L (66%) H-2 \rightarrow L+1 (17%) H \rightarrow L+1 (17%)
4a	360	351	0.596 (S17)	H-3 \rightarrow L+1 (56%) H-4 \rightarrow L+2 (34%) H-3 \rightarrow L+2 (17%)
	409	479	0.194 (S3)	H-2 \rightarrow L (68%)



means the main charge transfer are along the z and x-axis. It is found that the β_{tot} values of v shaped complexes are larger than the linear complex **1a**. Among the studied complexes, the complex **2a'** has the largest β_{tot} value, which is about 800 times larger than the

Based on the analysis of the electron transition property, a high degree of intramolecular charge-transfer should occur, and a large second-order NLO response could be expected for our studied complexes. The static first hyperpolarizability was calculated at the CAM-B3LYP/6-31+G* level of theory and listed in Table 2. Among these components, the main components are β_{xxz} and β_{zzz} , which

Complex	β_{XXZ}	β_{ZZZ}	$\mu(\beta_{\text{XXZ}}/\beta_{\text{ZZZ}})$	β_{tot}
1a	6.668	13.195	0.505	20.372
2a	14.450	43.075	0.335	51.130
2a'	35.261	75.830	0.464	102.717
3a	-8.267	14.329	-0.577	40.051
4a	-28.418	-21.264	1.336	42.017

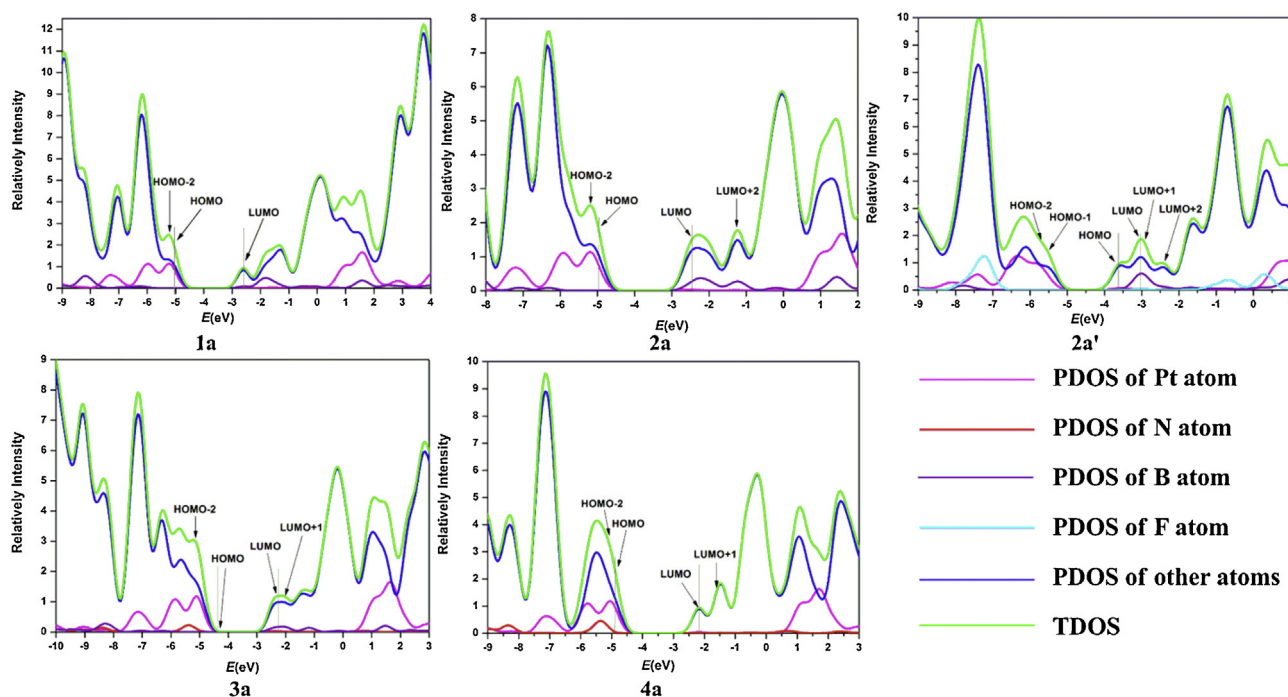


Fig. 4. The total density of states (TDOS) and the partial density of states (PDOS) calculation of all the complexes.

first hyperpolarizability of the organic urea molecule [14] and 24 times larger than that measured for highly π -delocalized phenyliminomethyl ferrocene complex [55]. Thus, the studied complexes exhibit excellent second-order nonlinear optical response.

The charge transfer of the v shaped complexes is along both the z and x axis, these complexes may exhibit two-dimensional (2D) NLO response. Thus, the first hyperpolarizability anisotropy ratio μ (β_{zyy}/β_{zzz}) was used to check the 2D NLO response [56]. It is noted that the μ value is very sensitive to the off-diagonal components and a relative parameter to describe the 2D character of molecules NLO responses [57]. When the μ value is less than or equal to 0.1, these complexes exhibit predominantly 1D NLO response [56]. From Table 2, it can be seen that μ values of the studied complexes are large than 0.1. That is, all the complexes possess a 2D NLO response.

Oudar and Chemla established a two-level model to rationalize the origin of β_{tot} value for a low-lying transfer transition [58,59].

$$\beta_0 \propto \frac{3\Delta\mu f_0}{2\Delta E^3} \quad (4)$$

In the two-level model, the β_{tot} value is proportional to the dipole moments difference ($\Delta\mu$) between the ground state and the crucial excited state, and the oscillator strength (f_{os}), but inversely proportional to the third power of the transition energy (ΔE). From Table 3, it is found that the values of ΔE and f_{os} for all the complexes are nearly the same, which means that the trend of β_{tot} cannot be explained by using the two parameters. Thus, we calculated $\Delta\mu \cdot f_{\text{os}} / \Delta E^3$ (Table 3). It is interesting to find that the trend of β_{tot} value and $\Delta\mu \cdot f_{\text{os}} / \Delta E^3$ is the same (Fig. 5). Therefore, the

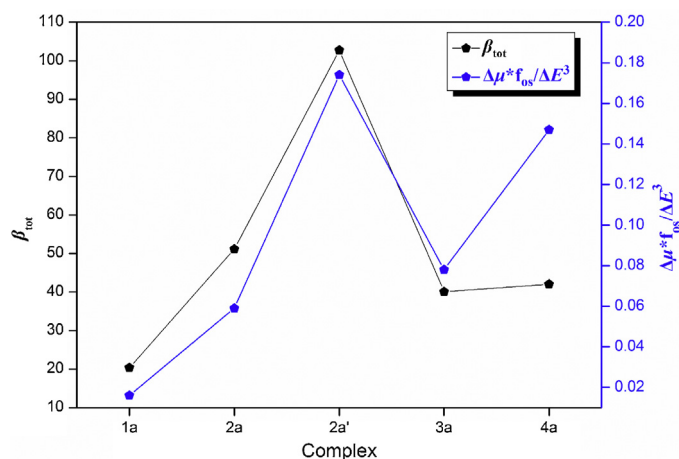


Fig. 5. Relationship between the first hyperpolarizabilities (β_{tot}) and the values of $\Delta\mu \cdot f_{\text{os}} / \Delta E^3$.

variation of first hyperpolarizabilities of the studied complexes can be explained by the combined effect of $\Delta\mu$, f_{os} and the cube of ΔE .

4. Conclusions

In this work, we investigated the photophysical properties of the Pt(II) triarylborons with a 2,2'-bpy core derivatives by using DFT method. The results show that the studied complexes exhibit an intense and weak absorption bands. The MLCT transition is mainly responsible for the low-energy absorption band with relative smaller oscillator strength, while the high-energy absorption band mainly derives from ILCT and LLCT transition. The electron absorption peaks are not only dependent on position of the Ph-BMes₂ but also on the electron-accepting ability of the acceptor groups. For the first hyperpolarizabilities, the β_{tot} value of v shaped complexes are larger than that of the linear complex, demonstrating the v shaped complexes have a possibility to be excellent second-order nonlinear optical material. For the standpoint of

Table 3

The difference between the ground and excited state transition dipole moments ($\Delta\mu$), transition energy (ΔE), oscillator strength (f_{os}) and the values of $\Delta\mu \cdot f_{\text{os}} / \Delta E^3$.

Complex	1a	2a	2a'	3a	4a
$\Delta\mu$ (Debye)	6.900	6.615	15.641	6.995	13.100
ΔE (eV)	2.400	2.438	2.073	2.480	2.586
f_{os}	0.033	0.129	0.099	0.169	0.194
$\Delta\mu \cdot f_{\text{os}} / \Delta E^3$	0.016	0.059	0.174	0.078	0.147

the two-level model, the first hyperpolarizabilities were correlated with the combined effect of the difference of dipole moment between the ground state and excited state, the oscillator strength and the cube of the transition.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jmgm.2013.07.006>.

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