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-BMes$_2$ 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.

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 bathochromatic 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 ($BMes_2$) group is considered to be an electron acceptor comparable in strength to the CN group [34,35]. Using the $BMes_2$ group as an electron acceptor, the donor–acceptor compounds might exhibit excellent nonlinear optical response. Additionally, the Mes group of $BMes_2$ can be replaced by the C_6F_5 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*-BMes_2-phenyl)_2-2,2′-bpy (Pt (5,5′-BP2bpy) Ph$_2$, **1a**), 4,4′-(*p*-BMes_2-phenyl)_2-2,2′-bpy (Pt (4,4′-BP2bpy) Ph$_2$, **2a**), 4-(*p*-BMes_2-phenyl)-4′-(*p*-NPh_2-phenyl)-2,2′-bipy (Pt (4,4′-BPNPbpy) Ph$_2$, **3a**), and 4,4′-(*p*-NPh_2-phenyl)_2-2,2′-bpy (Pt (4,4′-NP2bpy)Ph$_2$, **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 NPh$_2$ 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:

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

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(BNbpy)Ph$_2$ [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-BMes$_2$ 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 (CH_2Cl_2) solvent, the above calculation for complex **1a** was repeated under
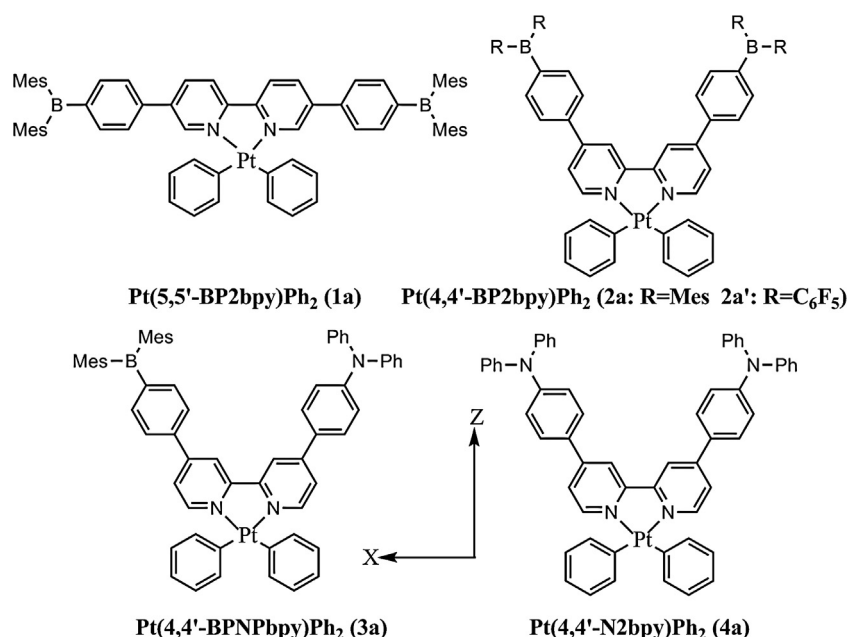
Fig. 1. The chemical structures and the axes convention used in theoretical calculations.

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 BMes$_2$ 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(C$_6$F$_5$)$_2$ 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 NPh$_2$ 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	$\lambda_{max,exp}$	$\lambda_{max,cal,gas}$	f_{os}	Transition nature
1a	369	380	0.948 (S14)	H-8 → L (58%) H-6 → L (17%) H-15 → L (17%)
	468	517	0.033 (S3)	H-2 → L (70%)
2a	330	368	0.346 (S14)	H-3 → L+1 (55%) H-6 → L (29%) H-5 → L+1(24%)
	460	508	0.129 (S3)	H-2 → L (66%) H → L+1(17%) H-2 → L+2(13%)
2a′		418	0.201 (S16)	H-6 → L (65%) H-5 → L+1 (18%) H-6 → L+2 (16%)
		598	0.099 (S4)	H-2 → L (63%) H-1 → L+1(25%) H-2 → L-2 (13%)
3a	345	363	0.201 (S17)	H-4 → L+1 (43%) H-9 → L (25%) H-6 → L+1 (23%)
	418	500	0.169 (S3)	H-2 → L (66%) H-2 → L+1(17%) H → L+1(17%)
4a	360	351	0.596 (S17)	H-3 → L+1 (56%) H-4 → L+2 (34%) H-3 → L+2 (17%)
	409	479	0.194 (S3)	H-2 → L (68%)
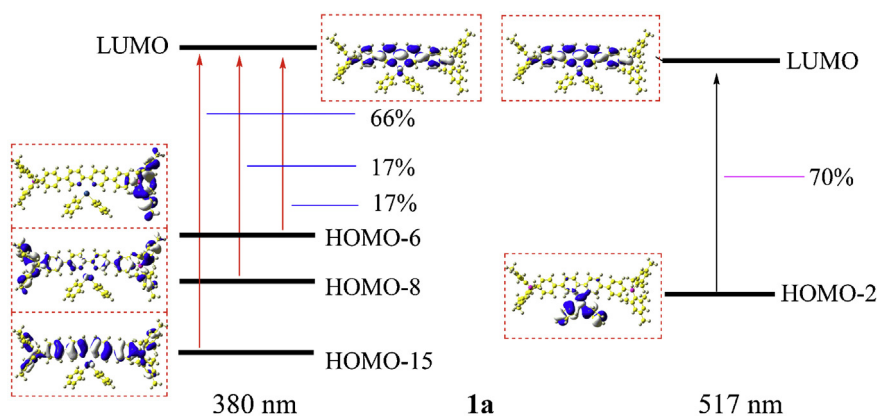
Fig. 2. Frontier molecule orbitals involved in crucial electronic excitations of complex **1a** by TD-PBE1PBE/6-31+G* method.
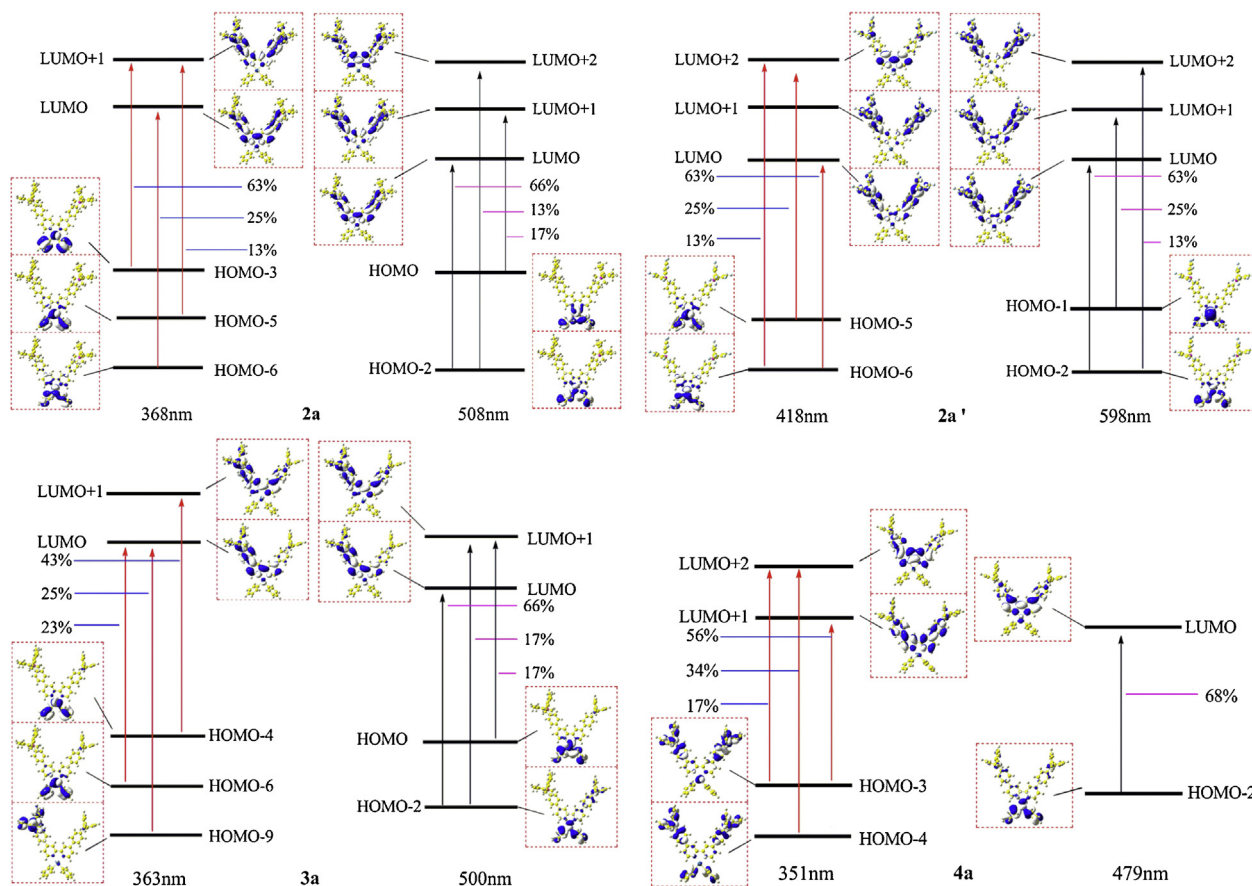

Fig. 3. Frontier molecule orbitals involved in crucial electronic excitations of selected complexes by TD-PBE1PBE/6-31+G* method.

and the B atoms makes almost thirty percent (27.70%) contribution to the LUMO orbital. which demonstrate that the introduction of C_6F_5 changes the contribution of different atom, and this change may be helpful for enhancing the first hyperpolarizability.

3.3. Static first hyperpolarizability

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

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

Table 2
The calculated first hyperpolarizabilities ($\times 10^{-30}$ esu) of the studied complexes by CAM-B3LYP/6-31+G* level of theory.

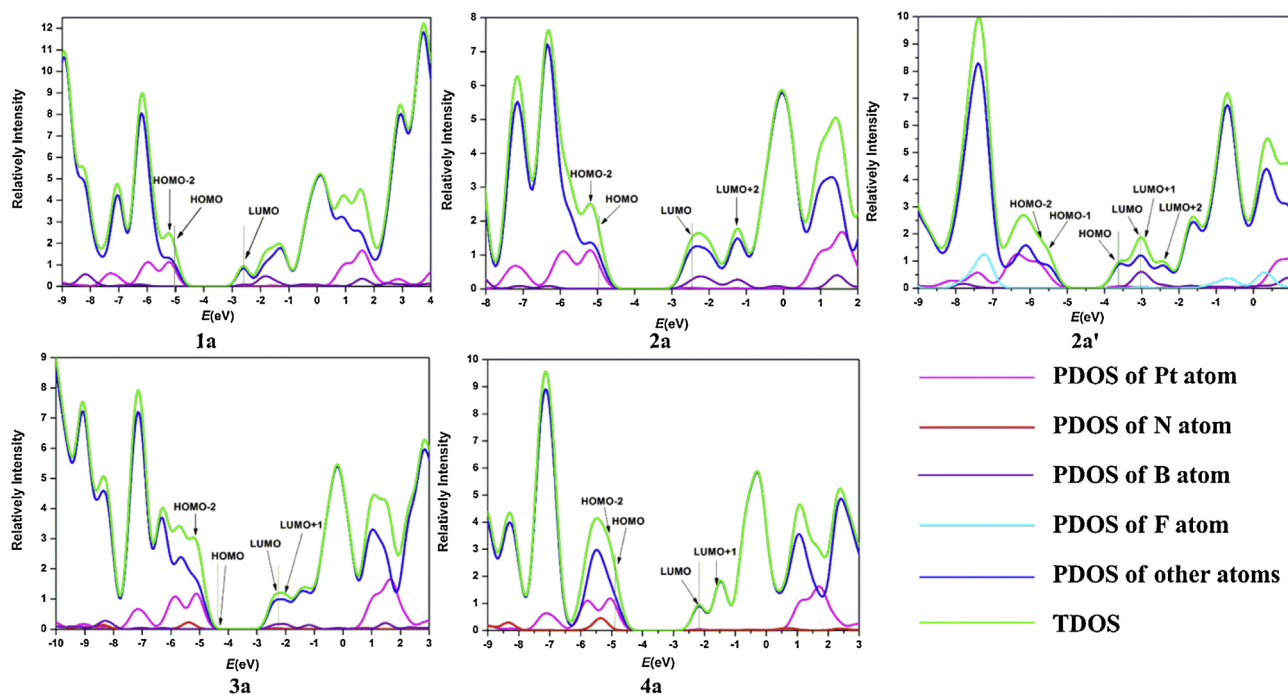| Complex	β_{xxz}	β_{zzz}	$\mu(\beta_{xxz}/\beta_{zzz})$	β_{tot}
1a	6.668	13.195	0.505	20.372
2a	14.450	43.075	0.335	51.130
2a′	35.261	75.830	0.464	102.717
3a	−8.267	14.329	−0.577	40.051
4a	−28.418	−21.264	1.336	42.017

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].

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

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 $\Delta\mu * f_{os}/\Delta E^3$ (Table 3). It is interesting to find that the trend of β_{tot} value and $\Delta\mu * f_{os}/\Delta E^3$ is the same (Fig. 5). Therefore, the

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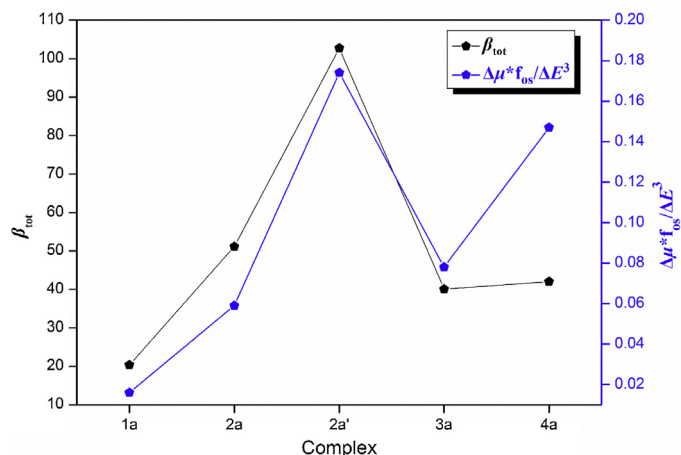The difference between the ground and excited state transition dipole moments ($\Delta\mu$), transition energy (ΔE), oscillator strength (f_{os}) and the values of $\Delta\mu * f_{os}/\Delta E^3$.

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
$\Delta\mu * f_{os}/\Delta E^3$	0.016	0.059	0.174	0.078	0.147

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

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-BMes$_2$ 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

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.

Acknowledgements

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.

References

[1] L.-A. Schaper, S.J. Hock, W.A. Herrmann, F.E. Kühn, Synthesis and application of water-soluble NHC transition-metal complexes, Angewandte Chemie International Edition 52 (2013) 270–289.

[2] M.R. Grochowski, T. Li, W.W. Brennessel, W.D. Jones, Competitive carbon—sulfur vs. carbon—carbon bond activation of 2-cyanothiophene with [Ni(dippe)H]₂, Journal of the American Chemical Society 132 (2010) 12412–12421.

[3] S. De Ornellas, T.E. Storr, T.J. Williams, C.G. Baumann, I.J.S. Fairlamb, Direct C–H/C–X coupling methodologies mediated by Pd/Cu or Cu: an examination of the synthetic applications and mechanistic findings, Current Organic Synthesis 8 (2011) 79–101.

[4] B.J. Coe, S.P. Foxon, E.C. Harper, M. Helliwell, J. Raftery, C.A. Swanson, B.S. Brunschwig, K. Clays, E. Franz, J. Garin, J.s. Orduna, P.N. Horton, M.B. Hursthouse, Evolution of linear absorption and nonlinear optical properties in V-shaped ruthenium(II)-based chromophores, Journal of the American Chemical Society 132 (2010) 1706–1723.

[5] N.J. Long, C.K. Williams, Metal alkynyl σ complexes: synthesis and materials, Angewandte Chemie International Edition 42 (2003) 2586–2617.

[6] M. Nakano, H. Fujita, M. Takahata, K. Yamaguchi, Theoretical study on second hyperpolarizabilities of phenylacetylene dendrimer: toward an understanding of structure–property relation in NLO responses of fractal antenna dendrimers, Journal of the American Chemical Society 124 (2002) 9648–9655.

[7] B.J. Coe, J. Fielden, S.P. Foxon, J.A. Harris, M. Helliwell, B.S. Brunschwig, I. Asselberghs, K. Clays, J. Garin, J.s. Orduna, Diquat derivatives: highly active, two-dimensional nonlinear optical chromophores with potential redox switchability, Journal of the American Chemical Society 132 (2010) 10498–10512.

[8] P. Hrobarik, P. Zahradnik, W.M.F. Fabian, Computational design of benzothiazole-derived push–pull dyes with high molecular quadratic hyperpolarizabilities, Physical Chemistry Chemical Physics 6 (2004) 495–502.

[9] P. Hrobarik, I. Sigmundova, P. Zahradnik, P. Kasak, V. Arion, E. Franz, K. Clays, Molecular engineering of benzothiazolium salts with large quadratic hyperpolarizabilities: can auxiliary electron-withdrawing groups enhance nonlinear optical responses, Journal of Physical Chemistry C 114 (2010) 22289–22302.

[10] P. Hrobárik, V. Hrobáriková, I. Sigmundová, P. Zahradník, M. Fakis, I. Polyzos, P. Persephonis, Benzothiazoles with tunable electron-withdrawing strength and reverse polarity: a route to triphenylamine-based chromophores with enhanced two-photon absorption, Journal of Organic Chemistry 76 (2011) 8726–8736.

[11] D. Cornelis, E. Franz, I. Asselberghs, K. Clays, T. Verbiest, G. Koeckelberghs, Interchromophoric interactions in chiral X-type π-conjugated oligomers: a linear and nonlinear optical study, Journal of the American Chemical Society 133 (2011) 1317–1327.

[12] A. Bossi, E. Licandro, S. Maiorana, C. Rigamonti, S. Righetto, G.R. Stephenson, M. Spassova, E. Botek, B. Champagne, Theoretical and experimental investigation of electric field induced second harmonic generation in tetrathia[7]helicenes, Journal of Physical Chemistry C 112 (2008) 7900–7907.

[13] Y. Si, G. Yang, Photophysical properties of azaboradibenzo[6]helicene derivatives, Journal of Materials Chemistry C 1 (2013) 2354–2361.

[14] D.R. Kanis, M.A. Ratner, T.J. Marks, Design and construction of molecular assemblies with large second-order optical nonlinearities. Quantum chemical aspects, Chemical Reviews 94 (1994) 195–242.

[15] M. Yang, B. Champagne, Large off-diagonal contribution to the second-order optical nonlinearities of λ-shaped molecules, Journal of Physical Chemistry A 107 (2003) 3942–3951.

[16] S. Di Bella, Second-order nonlinear optical properties of transition metal complexes, Chemical Society Reviews 30 (2001) 355–366.

[17] B.J. Coe, J.A. Harris, B.S. Brunschwig, I. Asselberghs, K. Clays, J. Garin, J. Orduna, Three-dimensional nonlinear optical chromophores based on metal-to-ligand charge-transfer from ruthenium(II) or iron(II) centers, Journal of the American Chemical Society 127 (2005) 13399–13410.

[18] O. Maury, H. Le Bozec, Molecular engineering of octupolar NLO molecules and materials based on bipyridyl metal complexes, Accounts of Chemical Research 38 (2005) 691–704.

[19] B.J. Coe, J.A. Harris, L.A. Jones, B.S. Brunschwig, K. Song, K. Clays, J. Garin, J. Orduna, S.J. Coles, M.B. Hursthouse, Syntheses and properties of two-dimensional charged nonlinear optical chromophores incorporating redox-switchable cis-tetraammineruthenium(II) centers, Journal of the American Chemical Society 127 (2005) 4845–4859.

[20] N. Gauthier, G. Argouarch, F. Paul, L. Toupet, A. Ladjarafi, K. Costuas, J.-F. Halet, M. Samoc, M.P. Cifuentes, T.C. Corkery, M.G. Humphrey, Electron-rich iron/ruthenium arylalkynyl complexes for third-order nonlinear optics: redox-switching between three states, Chemistry- A European Journal 17 (2011) 5561–5577.

[21] C.-G. Liu, Y.-Q. Qiu, S.-L. Sun, H. Chen, N. Li, Z.-M. Su, DFT study on second-order nonlinear optical properties of a series of mono Schiff-base M(II) (M = Ni, Pd, Pt) complexes, Chemical Physics Letters 429 (2006) 570–574.

[22] M. Bruschi, P. Fantucci, M. Pizzotti, Tailoring transition metal complexes for nonlinear optics applications. 2. A theoretical investigation of the second-order nonlinear optical properties of M(CO)(5)L complexes (M = Cr, W; L = Py, PyCHO, Pyz, PyzBF(3), BPE, BPEBF(3)), Journal of Physical Chemistry A 109 (2005) 9637–9645.

[23] P.G. Lacroix, Second-order optical nonlinearities in coordination chemistry: the case of bis(salicylaldiminato)metal Schiff base complexes, European Journal of Inorganic Chemistry (2001) 339–348.

[24] M. Asghari-Khiavi, F. Safinejad, Theoretical studies on metal porphyrin halides: geometrical parameters and nonlinear optical responses, Journal of Molecular Modeling 16 (2010) 499–503.

[25] N.N. Ma, G.C. Yang, S.L. Sun, C.G. Liu, Y.Q. Qiu, Computational study on second-order nonlinear optical (NLO) properties of a novel class of two-dimensional Λ- and W-shaped sandwich metallocarborane-containing chromophores, Journal of Organometallic Chemistry 696 (2011) 2380–2387.

[26] B.J. Coe, Switchable nonlinear optical metallochromophores with pyridinium electron acceptor groups, Accounts of Chemical Research 39 (2006) 383–393.

[27] B.J. Coe, N.R.M. Curati, E.C. Fitzgerald, S.J. Coles, P.N. Horton, M.E. Light, M.B. Hursthouse, Syntheses and properties of bimetallic chromophore-quencher assemblies containing ruthenium(II) and rhenium(I) centers, Organometallics 26 (2007) 2318–2329.

[28] C.-G. Liu, X.-H. Guan, Z.-M. Su, Computational study on redox-switchable 2D second-order nonlinear optical properties of push–pull mono-tetrathiafulvalene-bis(salicylaldiminato) Zn(II) Schiff base complexes, Journal of Physical Chemistry C 115 (2011) 6024–6032.

[29] Y. Si, G. Yang, Theoretical study on the photophysical properties of chiral mononuclear and dinuclear zinc complexes, RSC Advances 3 (2013) 2241–2247.

[30] Z.M. Hudson, S. Wang, Metal-containing triarylboron compounds for optoelectronic applications, Dalton Transactions 40 (2011) 7805–7816.

[31] J.C. Collings, S.Y. Poon, C. Le Droumaguet, M. Charlot, C. Katan, L.O. Palsson, A. Beeby, J.A. Mosely, H.M. Kaiser, D. Kaufmann, W.Y. Wong, M. Blanchard-Desce, T.B. Marder, The synthesis and one- and two-photon optical properties of dipolar, quadrupolar and octupolar donor–acceptor molecules containing dimesitylboryl groups, Chemistry – A European Journal 15 (2009) 198–208.

[32] C. Fan, L.G. Mercier, W.E. Piers, H.M. Tuononen, M. Parvez, Dihydrogen activation by antiaromatic pentaarylboroles, Journal of the American Chemical Society 132 (2010) 9604–9606.

[33] J.F. Blount, P. Finocchiaro, D. Gust, K. Mislow, Conformational analysis of triarylboranes, Journal of the American Chemical Society 95 (1973) 7019–7029.

[34] W. Kaim, A. Schulz, p-Phenylenediboranes: mirror images of p-phenylenediamines? Angewandte Chemie International Edition 23 (1984) 615–616.

[35] L. Weber, D. Eickhoff, T.B. Marder, M.A. Fox, P.J. Low, A.D. Dwyer, D.J. Tozer, S. Schwedler, A. Brockhinke, H.-G. Stammler, B. Neumann, Experimental and theoretical studies on organic D–π–A systems containing three-coordinate boron moieties as both π–donor and π–acceptor, Chemistry- A European Journal 18 (2012) 1369–1382.

[36] A. Sundararaman, F. Jäkle, A comparative study of base-free arylcopper reagents for the transfer of aryl groups to boron halides, Journal of Organometallic Chemistry 681 (2003) 134–142.

[37] H. Kameo, H. Nakazawa, Synthesis of a rhodium complex featuring the Rh–H–B linkage via a hydride migration from rhodium to borane: study on the electronic deviation induced by the presence of the boron moiety, Organometallics 31 (2012) 7476–7484.

[38] R.N. Grimes, Metal–carborane multidecker sandwich complexes as building blocks for new materials, Applied Organometallic Chemistry 10 (1996) 209–225.

[39] Y. Sun, S. Wang, Extending π-conjugation of triarylborons with a 2,2-bpy core: impact of donor–acceptor geometry on luminescence, anion sensing, and metal ion binding, Inorganic Chemistry 49 (2010) 4394–4404.

[40] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.

Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.

[41] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Physical Review Letters 77 (1996) 3865–3868.

[42] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Physical Review Letters 78 (1996) 1396.

[43] C. Adamo, V. Barone, Toward reliable density functional methods without adjustable parameters: the PBE0 model, Journal of Chemical Physics 110 (1999) 6158–6170.

[44] C. Adamo, V. Barone, Accurate excitation energies from time-dependent density functional theory: assessing the PBE0 model for organic free radicals, Chemical Physics Letters 314 (1999) 152–157.

[45] N.-N. Ma, S.-L. Sun, C.-G. Liu, X.-X. Sun, Y.-Q. Qiu, Quantum chemical study of redox-switchable second-order nonlinear optical responses of D–π–A system BNbpy and metal Pt(II) chelate complex, Journal of Physical Chemistry A 115 (2011) 13564–13572.

[46] M. Cossi, V. Barone, Solvent effect on vertical electronic transitions by the polarizable continuum model, Journal of Chemical Physics 112 (2000) 2427–2435.

[47] J. Lin, K. Wu, M. Zhang, A new hybrid DFT approach to electronic excitation and first hyperpolarizabilities of transition metal complexes, Journal of Computational Chemistry 30 (2009) 2056–2063.

[48] Y. Sun, S. Wang, Conjugated triarylboryl donor–acceptor systems supported by 2,2'-bipyridine: metal chelation impact on intraligand charger transfer emission, electron accepting ability, and "turn-on" fluoride sensing, Inorganic Chemistry 48 (2009) 3755–3767.

[49] A. Dreuw, M. Head-Gordon, Single-reference ab initio methods for the calculation of excited states of large molecules, Chemical Reviews 105 (2005) 4009–4037.

[50] D. Jacquemin, E.A. Perpete, G.E. Scuseria, I. Ciofini, C. Adamo, TD-DFT performance for the visible absorption spectra of organic dyes: conventional versus long-range hybrids, Journal of Chemical Theory and Computation 4 (2007) 123–135.

[51] Y. Liu, G.C. Yang, S.L. Sun, Z.M. Su, Density functional theory investigation on the second-order nonlinear optical properties of chlorobenzyl-O-carborane derivatives, Chinese Journal of Chemistry 30 (2012) 2349–2355.

[52] Y. Si, G. Yang, Z. Su, Chiroptical, linear, and second-order nonlinear optical properties of tetrathiafulvalenylallene: a multifunctional molecular material, Journal of Materials Chemistry C 1 (2013) 1399–1406.

[53] T.R. Cundari, H.A. Kurtz, T. Zhou, Computational study of polarizabilities and second hyperpolarizabilities of inorganic transition metal thiometalates and metalates in solution, Journal of Physical Chemistry A 104 (2000) 4711–4717.

[54] T.M. Inerbaev, R.V. Belosludov, H. Mizuseki, M. Takahashi, Y. Kawazoe, First excited state properties and static hyperpolarizability of ruthenium(II) ammine complexes, Journal of Chemical Theory and Computation 2 (2006) 1325–1334.

[55] S.K. Pal, A. Krishnan, P.K. Das, A.G. Samuelson, Schiff base linked ferrocenyl complexes for second-order nonlinear optics, Journal of Organometallic Chemistry 604 (2000) 248–259.

[56] S. Di Bella, I. Fragala, Two-dimensional characteristics of the second-order nonlinear optical response in dipolar donor–acceptor coordination complexes, New Journal of Chemistry 26 (2002) 285–290.

[57] P. Song, L.-K. Yan, W. Guan, C.-G. Liu, C. Yao, Z.-M. Su, A theoretical study on the efficient reversible redox-based switching of the second-order polarizabilities of two-dimensional nonlinear optical-active donor–acceptor phenanthroline-hexamolybdate, Journal of Molecular Graphics and Modelling 29 (2010) 13–20.

[58] J.L. Oudar, D.S. Chemla, Hyperpolarizabilities of the nitroanilines and their relations to the excited state dipole moment, Journal of Chemical Physics 66 (1977) 2664–2668.

[59] J.L. Oudar, Optical nonlinearities of conjugated molecules. Stilbene derivatives and highly polar aromatic compounds, Journal of Chemical Physics 67 (1977) 446–457.