Commun. Comput. Chem.
doi: 10.4208/cicc.2013.v1.n4.5

Vol.**1**, No.**4**, pp. 342-350
December 2013

## REGULAR ARTICLE

# Theoretical Investigation on Nonlinear Optical Properties of Novel O-carborane Derives

Jinling Cheng and Di Liu*

*State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China.*

Received 20 Sep 2013; Accepted (in revised version) 9 Oct 2013

**Abstract:** A calculation investigation using DFT/TDDFT methods on a series of o-carborane derives 1-6 has been performed on the molecular structures, lower transition energy, along with the nonlinear optical responses. Our theoretical calculations show that among the components, value of $\beta_y$ contributes the most to $\beta_{tot}$ for all these studied compounds which indicates that the main CT within the molecular along the y-axis direction. Moreover, the static first hyperpolarizability ($\beta_{tot}$) values as well as the ground state dipole moment ($\mu_g$) gradually increase with increasing donating ability of group. Further, the TDDFT studies suggest that the excited transition energy experiences a decline trend and a redshift occurs on the absorption spectrum. Our studies demonstrate that compound 6 can be used as excellent 2D second-order NLO materials from the standpoint of large $\beta_{tot}$, large $\mu_g$ values and low excited energy.

**AMS subject classifications:** 65D18, 74E40, 78M50, 82D99

**Keywords**: Nonlinear optics properties, O-carborane clusters, DFT/TDDFT, First hyperpolarizability

In the past few decades, the searches for luminescent materials were continuously expanding, and the nonlinear optical (NLO) materials have attracted significant interests of experimental and theoretical chemists due to their large nonlinear optical coefficient, fast nonlinear optical response times and relatively low cost [1-10]. Numerical investigations have been carried out to develop the nonlinear optical compounds, especially for the organic or

---

[*] Corresponding author *E-mail address*: liudi@dlut.edu.cn (D. Liu)

http://www.global-sci.org/cicc

metallorganics-based materials [6-7, 10]. A number of organic compounds with relatively enhanced second-order responses have been synthetized or uncovered [1, 9-12]. Recently, Martín group has proved the usefulness of tetrathiafulvalene (TTF) and ð-extended TTFs as NLO-phores and different TTF-based push-pull chromophores; moreover, Elangovan has reported the synthesis of bis-(4-methoxyphenyl) hetero-aryl-amino donor-based chromophores and their electrooptic activites [13, 14]. It is well known that typical second-order NLO is consisted by two crucial factors: one is a large polarizable π-conjugated unit, and the other is the conjoint donor or acceptor groups [8, 9]. The first hyperpolarizability (β) is the most important parameter to demonstrate the performance of the NLO materials which can be increased by introducing the multiple donor (D) and/or acceptor (A) groups [6, 8-9,13-17].

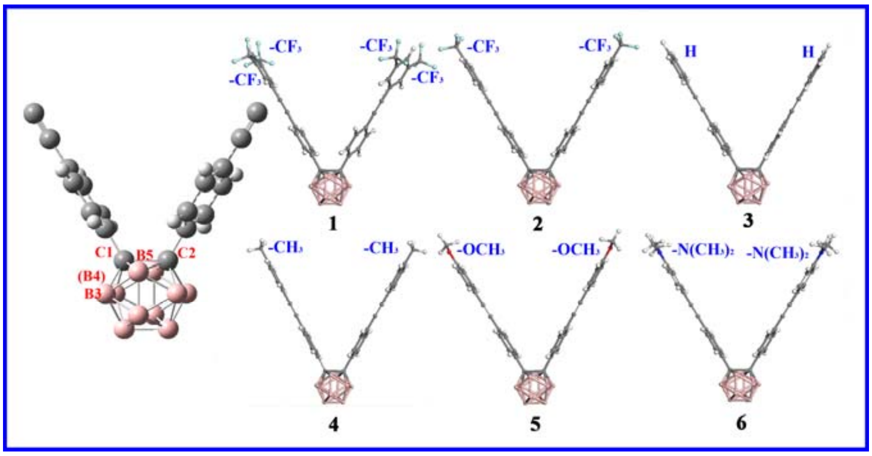

**Figure1**: Optimized structures of the investigated compounds 1-6 calculated by B3LYP/6-31+G (d,p)

O-Carborane ($C_2B_{10}H_{12}$) clusters exhibit remarkable thermal stability, and have been found to be one extremely qualified candidate for studying the nonlinear optical characters [17-22]. The carbon and boron atoms of the cage are shown in **Fig.1**, as it demonstrated that these carboranes have icosahedral geometry, in which the carbon and boron atoms are tricoordinate. This structural feature can contribute to the stability of such molecules and their derivatives. In 2010, a family of 2D molecules centered with o-Carborane was synthesized by Chujo et al [22]. In this system, the electron-donating or the electron-withdrawing groups are attached to the o-carborane cage via arylacetylenes π-conjugation, which is considered to have strong electron-withdrawing property. On the one hand, those emission properties that can be effectively justified by changing the electronic-donating and electronic-withdrawing substitutions, on the other, the intramolecular charge transfer (ICT) from π-conjugated units to o-carborane should play the other key role [14,21-24].

Based on above discussions, the various substitutions play a vital role in turning the ICT characters which subsequently justifies the NOL properties. However, the NLO responses of these groups introducing into o-carboranes remain unclear. On the basis of these opinions, the density functional theoretical method (DFT) and time dependent density functional theoretical method (TDDFT) were employed to investigate different o-carborane molecules with electron-withdrawing and electron-donating substituents to tune the NLO activity.

Geometrical optimization of the studied compounds was carried out with the B3LYP/6-31G + (d, p) combinations of DFT without any symmetry constraint and all these results can reach a well agreement with the crystal structures which can reflect the reliability and accuracy of the selected methods [8-10]. Meanwhile, TDDFT method was employed to calculate the absorption spectra of the studied molecules as well as the excited energy. According to Suponitsky's results, B3LYP/6-31G+(d,p) can lead to a correct semi-quantitative description on the hyperpolarizabilities [25]. A self-consistent reaction field approach (SCRF) and the polarizable continuum model (PCM) was used to imitate the solvent effect on molecular geometries, absorption spectra and first hyperpolarizabilities as well.[26] In the present paper, the calculation formula of first hyperpolarizability $\beta_{tot}$ is defined as fellows[9-10, 27-28]:

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \text{ and } \mu = \beta_{yyy} + \beta_{xxy} + \beta_{yzz} \qquad (1)$$

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

All the calculations were carried out using the GAUSSIAN 09W program package [9].

**Table 1** Selected bond lengths (Å), bond angle θ (º) formed by two branches and dihedral angle ϕ (º) between the two π-conjugations values at the B3LYP/6-31G+(d,p) and the experiment dates from the ref. [21] shown in the braces.

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| C1-C2 | 1.776 | 1.767(1.727) | 1.768(1.726) | 1.777(1.725) | 1.778(1.737) | 1.789 |
| C1-B3 | 1.707 | 1.708(1.712) | 1.709(1.720) | 1.706(1.714) | 1.705(1.707) | 1.705 |
| C1-B5 | 1.722 | 1.725(1.742) | 1.724(1.730) | 1.722(1.739) | 1.723(1.724) | 1.722 |
| B3-B5 | 1.777 | 1.778(1.775) | 1.778(1.775) | 1.777(1.776) | 1.778(1.781) | 1.778 |
| θ | 58.85 | 59.35(55.12) | 59.17(59.39) | 58.86(58.65) | 59.23(56.74) | 58.87 |
| ϕ | 1.49 | 0.00(0.28) | 1.55(1.52) | 1.50(1.87) | 1.43(1.60) | 1.387 |

The optimized geometry structures have been obtained using density functional theory (DFT) at 6-311+(2d,2p) and Becke's three-parameter hybrid exchange function with Lee-Yang-Parr gradient-corrected correlation functional (B3LYP) level and shown in **Fig. 1.** The frameworks are constructed by different substitutions and o-carborane via a π-conjugated bridge: arylacetylene. It should be noted that the o-carborane cluster is electron-deficient as the vacant p-orbital of B atom, on the other hand the introduced groups conduct different electronic performances, for compounds 1 and 2, the electronic-withdrawing groups 3,5-bis(trifluoromethyl)phenyl and 4-trifluoromethylphenyl are used to form a A–p–A–p–A mode while electronic-donating groups 4-methyoxylphenyl and 4-dimethylaminophenyl to investigate push-pull effects (4 and 5), and compound 3 is designed just to extend the π-conjugation. From the structures, we can draw that the locations of 1 and 2 atoms is equivalent as well as that of 3 and 4 atoms.

The selected bond lengths (number of atoms, see **Fig. 1**), the dihedral angle $\phi$ between the π-conjugation and the $\theta$ formed by the line passing through two branches of optimized structures are listed in **Table 1** with the corresponding crystal data from the reference [21]. The agreement between the calculated data and the practical experimental data means that the current method is suitable for this study. Researches shows that a larger $\theta$ tends to generate a large off-diagonal component while the smaller one tends to generate a large diagonal component [29]. In our studies, the angle is 58.85° for compound 1 which is connected with neither electronic-withdrawing nor electronic-donating groups, whereas increases for compounds 2-6. Moreover, the replacement of phenyl with 3, 5-bistrifluoromethylphenyl and 4-trifluoromethyl leads the band length of C1-C2 decreased form 1.776 for compound 1, 1.767 for compound 2 and 1.768 for compound 3. With the increasing electronic-donating ability, the bond lengths of C1-C2 enlarge for compounds 3-5. While for the bond lengths of C1-C2, the changed trend happens to reversed as lengthened for compound 1-2 and decreased for the others. For the other parameters, the changing trend is ambiguous for band length of C1-B5 and B3-B5, nevertheless, extremely difference for the dihedral angle $\phi$ between the two π-conjugations as the data is zero in compound 1.

**Table 2** The calculated ground state dipole moment ($\mu_g$, a.u.) and static hyperpolarizabilities ($10^{-30}$ esu) of all molecules.

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $\mu_g$ | 1.0024 | 1.9068 | 9.6375 | 10.6161 | 6.8625 | 10.3679 |
| $\beta_x$ | 0.037 | 10.80 | -0.26 | 0.51 | 3.75 | 2.76 |
| $\beta_y$ | 4.98 | 26.05 | -108.85 | 154.64 | 128.72 | 240.17 |
| $\beta_z$ | 0.03 | 0.002 | -0.05 | -0.10 | -0.78 | -0.30 |
| $\beta_{tot}$ | 4.99 | 26.06 | 108.90 | 155.06 | 129.06 | 240.30 |

According to the former studies, the dipole moment, polarizability, the first-order hyperpolarizabilities characterize the NLO response and the structure-property relationship which consequently determine the response of the system in the applied electronic field.[1-10] The ground state dipole moment ($\mu_g$) mostly depends on the strength of D/A groups, the polarizabilities mainly reflects the molecular interactions and the hyperpolarizabilities is the essential measurements of the NLO character [30]. From **Table 2**, we can drawn that the $\mu_g$ values have a tendency to increase from compound 1 to 6, which indicts that $\mu_g$ can be turned by changing the strength of donor groups. Then, the calculated values of static first hyperpolarizability are also tabulated in **Table 2** including $\beta_x$, $\beta_y$, $\beta_z$ and $\beta_{tot}$. Among the three components ($\beta_x$, and $\beta_z$), the components value of $\beta_y$ is much close to the $\beta_{tot}$ for all these studied compounds, which indicates that the main CT within the molecular is along the y-axis direction. Moreover, according to the $\beta_{tot}$ of compounds 4-6, the introduction of electron donor groups can increase the first hyperpolarizabilities compared with acceptor (compound 1 and 2) and phenyl groups (compound 3) [ 10, 31-32]. For example, the $\beta_{tot}$ value of compound 6 is about 48 times larger than that of compound 1, and 10 times when compared with compound 3. This might attribute to the large electronegativity of o-carborane cluster which can constructer the electronic pushing-pulling system. Overall, compound 6, shows the largest first hyperpolarizability and may conduct as the promising candidates in the second-order NLO fields.

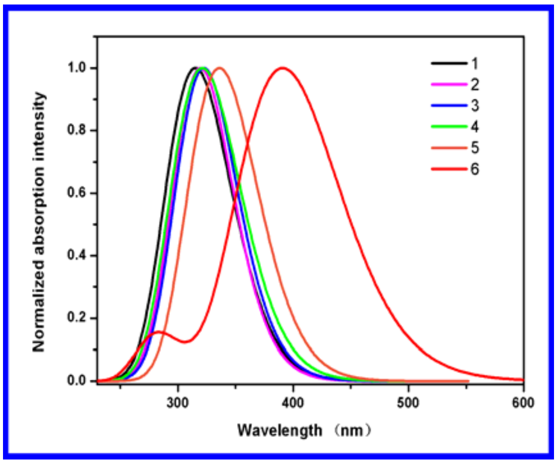

**Figure 2**: Normalized absorption spectrums of investigated compound 1-6, carried out by TDDFT calculation using B3LYP/6-31+G (d,p).

It has been reported that some o-carborane derivatives exhibit potential application in luminescent sensors. To reveal the origin of the spectrum response in these studied molecules, the electric transition properties are calculated and listed in **Table 3** and the electronic spectra is given out as well. From **Fig. 2**, we can see that all of these molecules show an intense absorption peak from 300 nm to 350 nm except the compound 6. The strong electronic-donating group $-N(Me)_2$ reduces the excited energy dramatically yielding a redshift of absorption spectra peaking at 380 nm. Related papers have shown that the $\beta_{tot}$ value varies inversely with the cube of transition energy (E), so the key factor in determining first hyperpolarizability is the low transition energy. In other word, the smaller the transition energy is, the larger first hyperpolarizability will be. We can speculate that the compound 6 can perform better NLO properties based on our calculated results and the former conclusions. Molecular orbital (MO) analysis can directly provide insight into the nature of the electronically excited states and the frontier molecular orbitals (MOs) of the monomer are demonstrated in **Fig. 3**. Herein, only HOMO and LUMO+1 are presented of all these compounds, since the excited state with the largest oscillation strength is mainly attributed to the transition of HOMO→LUMO+1. As it is depicted in **Fig. 3**, the electron transition mainly concentrates upon the π-conjugated bridge which means the local-exciting (LE), however, as the electron-donating ability of the introduced group increased, the electronic density on o-carborane increases at the same time. The MOs analysis can demonstrate that strong electronic-donating group can bridge electronic pushing and pulling channel with the o-carborane indirectly and also reach an agreement with above first hyperpolarizabilities results [33].

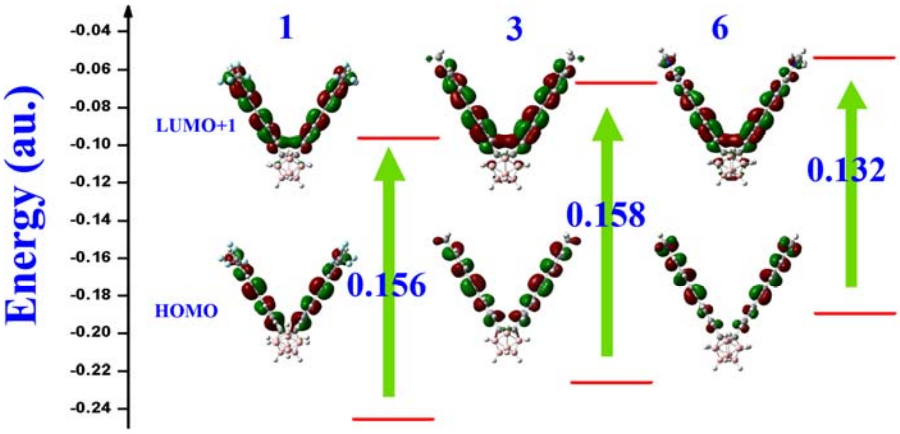

**Figure 3**: Frontier molecular orbits and computed energy levels of compound 1, 3 and 6, calculated with DFT/TDDFT at the B3LYP/6-31+G(d) level using Gaussian 09.

Density functional theory calculation has been performed on the nonlinear optical properties of a series of o-carboranes derivatives (1-6) with the arylacetylenes as π-conjugation bridge. On the basis of studied results of absorption spectra, dipole moment, excited transition energy and the first hyperpolarlizabilities, it can be demonstrated that increasing the strength of donor groups in the end of the π bridge could result in large $\beta_{tot}$ values and redshift of the absorption spectra. Importantly, the charge transfer from the π-conjugation and donating group to o-caborane cluster is helpful for second-order NLO responses. Our researches reveal that these complexes can be used as excellent 2D second-order NLO materials, especially the compound 6 as it displays the larger high transparency and β values.

**Table 3** The calculated transition energy ($\lambda_{max}$, nm), oscillator strength (*f*) and corresponding dominant MO transition nature of the studied compounds derivatives 1-6 calculated by B3LYP/6-31+G (d,p).

| molecular | Transition state | $\lambda_{\text{max}}$ (nm) | *f* | Transition nature |
|---|---|---|---|---|
| 1 | S0→S3 | 319.49 | 1.0670 | HOMO ->LUMO+1 |
| 2 | S0→S4 | 322.49 | 1.1663 | HOMO ->LUMO+1 |
| 3 | S0→S4 | 315.23 | 1.1876 | HOMO ->LUMO+1 |
| 4 | S0→S4 | 321.16 | 1.2103 | HOMO ->LUMO+1 |
| 5 | S0→S4 | 336.63 | 1.0669 | HOMO ->LUMO+1 |
| 6 | S0→S4 | 380.88 | 1.0559 | HOMO ->LUMO+1 |

## References

[1] S.R. Marder, Organic nonlinear optical materials: where we have been and where we are going, Chem. Commun., 2006, 131–134.

[2] M.G. Kuzyk, Using fundamental principles to understand and optimize nonlinear-optical materials, J. Mater. Chem., 19 (2009), 7444–7465.

[3] D. Locatelli, S. Quici, D. Roberto, F. De Angelis, The unexpected similar secondorder NLO re sponse for nearly planar and largely twisted push–pull stilbazole chromophores: EFISH and theoretical TD-DFT evidence, Chem. Commun., 2005, 5405–5407.

[4] H. Kang, A. Facchetti, H. Jiang, E. Cariati, S. Righetto, R. Ugo, C. Zuccaccia, A. Macchioni, C.L. Stern, Z. Liu, S.-T. Ho, E.C. Brown, M.A. Ratner, T.J. Marks, Ultralarge hyperpolarizability twisted p-electron system electro-optic chromophores: synthesis, solid-state and solution-phase structural characteristics, electronic structures, linear and nonlinear optical properties, and computational studies, J. Am. Chem. Soc., 129 (2007), 3267–3286.

[5] J.L. Bredas, C. Adant, P. Tackx, A. Persoons, B.M. Pierce, Third-order nonlinear optical response in organic materials: theoretical and experimental aspects, Chem. Rev. 94 (1994) 243–278

[6] B.J. Coe, Switchable nonlinear optical metallochromophores with pyridinium electron acceptor groups, Acc. Chem. Res., 39 (2006), 383–393.

[7] Z.J. Zhou, X.P. Li, F. Ma, Z.B. Liu, Z.R. Li, X.R. Huang, C.C. Sun, Exceptionally large second-order nonlinear optical response in donor–grapheme nanoribbon–acceptor systems, Chem. Eur. J., 17 (2011), 2414–2419.

[8] M.L. McKee, Z.-X. Wang, P.V.R. Schleyer, Ab initio study of the hypercloso boron hydrides BnHn and BnHn-exceptional stability of neutral B13H13, J. Am. Chem. Soc., 122 (2000), 4781–4793.

[9] Y. Liu, G.C. Yang, S.L. Sun, Z.M. Su, Theoretical investigation on two-dimensional molecule-based second-order nonlinear optical materials of the disubstituted o-carborane derivatives, Comput. Theor. Chem., 992 (2012), 142–149.

[10] N.N Ma, L.K. Yan, W. Guan, Y.Q. Qiu, and Z.M. Su, Theoretical investigation on electronic structure

and second-order nonlinear optical properties of novel hexamolybdate-organoimido-(car)borane hybrid. Phys. Chem. Chem. Phys., 14 (2012), 5605–5612.

[11] Y.Y. Hu, S.L. Sun, R.L. Zhong, H.L. Xu, Z.M. Su, Novel trumpet-shaped conjugation bridge (carbon nanocone) for nonlinear optical materials, J. Phys. Chem. C 115 (2011) 18545–18551.

[12] W. Chen, Z. R. Li, D. Wu, Y. Li, C.C. Sun, F.L. Gu, Y. Aoki, Nonlinear Optical Properties of Alkalides Li+(calix[4]pyrrole)M- (M = Li, Na, and K): Alkali Anion Atomic Number Dependence. J. Am. Chem. Soc., 128 (2006), 1072-1073.

[13] B. Insuasty, C. Atienza, C. Seoane, N. Martín, J. Garín, J. Orduna, R. Alcalá, B. Villacampa, Electronic and structural effects on the nonlinear optical behavior in push–pull TTF/tricarbonyl chromiun arene complexes, J. Org. Chem., 69 (2004), 6986–6995.

[14] J.A. Davies, A. Elangovan, P.A. Sullivan, B.C. Olbricht, H.D. Bale, T.R. Ewy, R. Formation, Rational enhancement of second-order nonlinearity: bis-(4-methoxyphenyl) hetero-aryl-amino donor-based chromophores: design, synthesis, and electrooptic activity. J. Am. Chem. Soc., 130 (2008), 10565–10575.

[15] B.J. Coe, J.A. Harris, B.S. Brunschwig, Determination of the molecular quadratic non-linear optical responses of V-shaped metallochromophores by using stark spectroscopy, Dalton Trans. (2003) 2384–2386.

[16] R. Juarez, M. Ramos, J.L. Segura, J.S. Orduna, B.n. Villacampa, R. Alicante, Synthesis and electrochemical and theoretical studies of V-shaped donor–acceptor hexaazatriphenylene derivatives for second harmonic generation, J. Org. Chem., 75 (2010), 7542–7549.

[17] V.I. Bregadze, Dicarba-closo-dodecaboranes C2B10H12 and their derivatives, Chem. Rev., 92 (1992), 209–223.

[18] A.G. Douglass, K. Czuprynski, M. Mierzwa, P. Kaszynski, An assessment of carborane-containing liquid crystals for potential device application, J. Mater. Chem., 8 (1998), 2391–2398.

[19] P. Farràs, F. Teixidor, I. Rojo, R. Kivekäs, R. Sillanpää, P. González-Cardoso, C. Viñas, Relaxed but highly compact diansa metallacyclophanes, J. Am. Chem. Soc., 133 (2011), 16537–16552.

[20] M.A. Fox, K. Wade, Model compounds and monomers for phenylene ether carboranylene ketone (PECK) polymer synthesis: preparation and characterization of boron-arylated ortho-carboranes bearing carboxyphenyl, phenoxyphenyl or benzoylphenyl substituents, J. Mater. Chem., 12 (2002), 1301–1306.

[21] K. Kokado, Y. Chujo, Multicolor tuning of aggregation-induced emission through substituent variation of diphenyl-o-carborane, J. Org. Chem., 76 (2011), 316–319.

[22] K. Kokado, A. Nagai, Y. Chujo, Energy transfer from aggregation-induced emissive o-carborane, Tetrahedron Lett., 52 (2011), 293–296.

[23] B.J. Coe, J. Fielden, S.P. Foxon, M. Helliwell, B.S. Brunschwig, I. Asselberghs, K. Clays, J. Olesiak, K. Matczyszyn, M. Samoc, Quadratic and cubic nonlinear optical properties of salts of diquat-based chromophores with diphenylamino substituents, J. Phys. Chem. A, 114 (2010), 12028–12041.

[24] 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, J. Am. Chem. Soc. 132 (2010) 10498–10512.

[25] K.Y. Suponitsky, S. Tafur, A.E. Masunov, Applicability of hybrid density functional theory methods to calculation of molecular hyperpolarizability. J. Chem. Phys., 129 (2008), 044109.

[26] P.C. Ray, J. Leszczynski, Two-photon absorption and first nonlinear optical properties of ionic octupolar molecules: structure−function relationships and solvent effects, J. Chem. Phys. Lett., 399(2004), 6689-6690.

[27] F. Sim, S. Chin, M. Dupuis, J.E. Rice, Electron correlation effects in hyperpolarizabilities of p-nitroaniline, J. Phys. Chem., 97 (1993), 1158–1163.

[28] Z.J. Li, F.F. Wang, Z.R. Li, H. L. Xu, X. R. Huang, D. Wu, W. Chen, G. T. Yu, F.L. Gu, Y. Aoki, Large static first and second hyperpolarizabilities dominated by excess electron transition for radical ion pair salts M2[radical dot] + TCNQ[radical dot]-(M = Li, Na, K), Phys. Chem. Chem. Phys., 11 (2009), 402–408.

[29] G. Bourhill, J.-L. Bredas, L.-T. Cheng, S.R. Marder, F. Meyers, J.W. Perry, B.G. Tiemann, Experimental demonstration of the dependence of the first hyperpolarizability of donor–acceptor-substituted polyenes on the groundstate polarization and bond length alternation, J. Am. Chem. Soc., 116 (1994), 2619–2620.

[30] G. Maroulis, Static hyperpolarizability of the water dimer and the interaction hyperpolarizability of two water molecules, J. Chem. Phys., 113 (2000), 1813-1821.

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

[32] M. Yang, B. Champagne, Large off-diagonal contribution to the second-order optical nonlinearities of K-shaped molecules, J. Phys. Chem. A., 107 (2003), 3942–3951.

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