

The symmetric and asymmetric thiophene-fused benzocarborane: structures and first hyperpolarizabilities

Yong Li · Heng-Qing Wu · Hong-Liang Xu ·
Shi-Ling Sun · Zhong-Min Su

Received: 23 March 2013 / Accepted: 13 May 2013 / Published online: 22 June 2013
© Springer-Verlag Berlin Heidelberg 2013

Abstract The unusual properties of thiophene-fused benzocarborane have attracted a lot of interest in recent years due to their wide applications in photonics and optoelectronics. In the present work, nine molecules [M, N] (M, N are labeled as the number of thiophene rings on the left and right part, respectively) on the basis of thiophene-fused benzocarborane were considered. The first hyperpolarizability (β_{tot}) values of three synthesized symmetric molecules [1, 1], [2, 2], [3, 3] (M=N, Chem. Eur. J 2012. 18, 11251–11257) and six asymmetric molecules [1, 2], [1, 3], [1, 4], [1, 5], [2, 3], [2, 4] (M≠N) were investigated, β_{tot} values of symmetric molecules show the order: 39 of [1, 1] < 800 of [2, 2] < 903 au of [3, 3], which indicate that β_{tot} value increases with increasing the number of thiophene ring for symmetric molecules. The other order of β_{tot} values can be observed: 39 of [1, 1] < 800 of [1, 2] < 3553 of [1, 3] < 7998 of [1, 4] < 13049 au of [1, 5] and 66 of [2, 2] < 3240 of [2, 3] < 8029 au of [2, 4]. Interestingly, when sum of M and N is constant, larger difference between M and N is, larger β_{tot} value is: 800 au of [2, 2] < 3553 au of [1, 3]; 3240 au of [2, 3] < 7998 au of [1, 4]; 903 au of [3, 3] < 8029 au of [2, 4] < 13049 au of [1, 5]. Significantly, [1, 5] with six thiophene rings has the largest β_{tot} value (13049 au) which is greatly larger than 903 au of [3, 3] with six thiophene rings. Furthermore, the natural bond orbital (NBO) charge populations, the nucleus-independent chemical shift (NICS), the bond length alternation (BLA) of the nine molecules and crucial transition were studied in our work. We hope that the present work will be beneficial for future theoretical and experimental studies on

the electro-optical properties of thiophene-fused benzocarborane molecules.

Keywords Crucial transition energy · Density functional theory (DFT) · First hyperpolarizability · Nonlinear optical material · Thiophene-fused benzocarborane

Introduction

Due to enormous need of nonlinear optical (NLO) materials for the potential applications in the fields of photonics and optoelectronics [1–6], the prediction and understanding of hyperpolarizabilities of molecules have received increasing attention. So far, there are inorganic [7, 8] and organic NLO materials [9, 10], the organic materials are of major interest because of their low dielectric constants, fast time responses and high laser damage thresholds [11]. At the same time, many strategies based on organic materials have been proposed to enhance the NLO response, such as the introduction of acceptor/donor groups [2], the use of molecules with extended π -electron systems [3], twisted π -electron systems [12, 13], the planar donor- π -conjugated bridge-acceptor (D- π -A) [14], enhanced push-pull effects [15] and bond length alternation (BLA) [16].

Carboranes are a class of polyhedral boron cluster compounds containing two carbon atoms in the cluster cage. It has three-center two-electron bonds as well as three dimensionally conjugated electrons that confer high chemical and thermal stability [17, 18]. As a result of these special properties, some carborane compounds and their derivatives have been synthesized and reported. For example, Tour and co-workers exploited the highly symmetric structural features of carborane by employing it as a wheel [19, 20]. Yamamoto and co-workers synthesized carborane-fullerene by taking advantage of the strong electron-withdrawing character of carborane [21, 22]. In addition, our group have reported

Y. Li · H.-Q. Wu · H.-L. Xu · S.-L. Sun (✉) · Z.-M. Su (✉)
Institute of Functional Material Chemistry, Faculty of Chemistry,
Northeast Normal University, Changchun 130024, Jilin,
People's Republic of China
e-mail: sunsl430@nenu.edu.cn
e-mail: zmsu@nenu.edu.cn

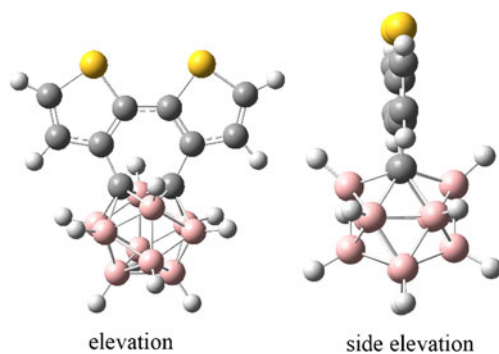
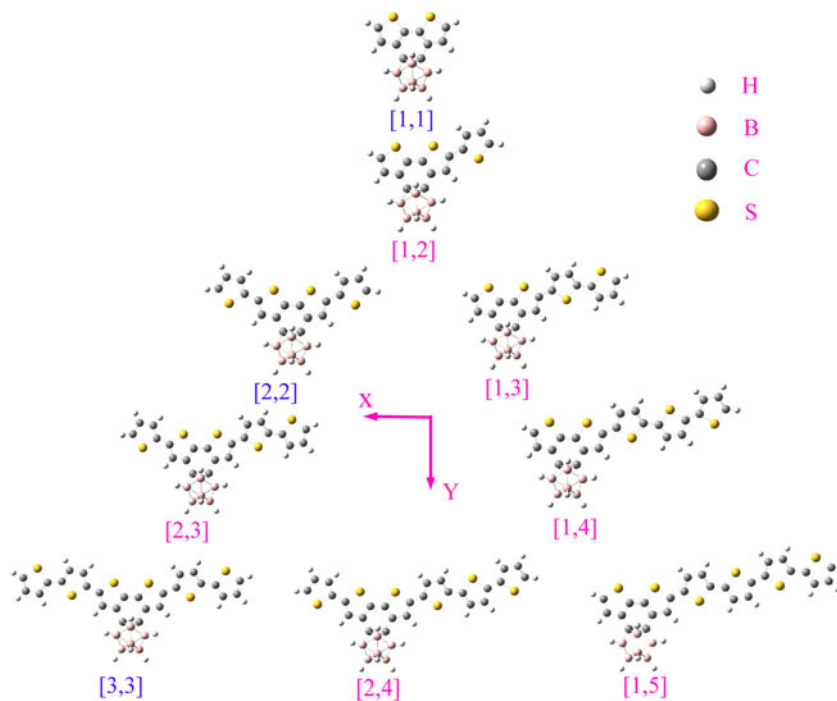


Chart 1 Structure of elevation and side elevation in [1, 1]

theoretical investigation on two-dimensional molecule-based second-order nonlinear optical materials of the disubstituted o-carborane derivatives as well as the electronic structures and the second-order nonlinear optics properties of the o-carborane derivatives and elucidated structure–property relationships [23]. Recently, Morisaki has synthesized the thiophene-fused benzocarborane and its derivatives, as well as discussed its potential use as a building block for various o-carborane-based π -conjugated molecules, such as its crystal structure revealed high coplanarity and non-aromaticity for the center C_6 ring moiety, the facile transformation of benzocarano dithiophene enables us to prepare various π -conjugated oligomers and polymers [24]. However, the nonlinear optical properties of thiophene-fused benzocarborane molecules have scarcely been reported. What the differences of the static first hyperpolarizabilities between the symmetric and asymmetric configuration? Can molecules with two different configurations be considered as potential NLO materials candidates?

Fig. 1 The optimized structures of the nine molecules



In this work, nine molecules [M, N] (M, N are labeled as the number of thiophene rings on the left and right part, respectively) on the basis of thiophene-fused benzocarborane were considered. Three symmetric molecules [1, 1] (see Chart 1), [2, 2] and [3, 3] were synthesized by experiment [24], and other six asymmetric molecules [1, 2], [1, 3], [1, 4], [1, 5], [2, 3], [2, 4] were designed as shown in Fig. 1. Our investigation mainly focused on the static first hyperpolarizability, the structures, natural bond orbital (NBO) charge populations, the nucleus-independent chemical shift (NICS) and the bond length alternation (BLA).

Computational details

According to previously reported investigations, the density functional theory (DFT) method B3LYP has been widely used to optimize the geometries of molecules such as carboranes [24]. In addition, our results show that the optimized structure obtained by the B3LYP method is very similar to experimental results. Therefore, in the present work, optimized geometries with all real frequencies were obtained at the B3LYP/6-31G** level.

Choosing a proper method to calculate the (hyper) polarizability of a system is crucial. The MP2 method is more reliable in calculating (hyper) polarizability, but it is quite costly for large computational costs. The B3LYP method has been reported to overestimate the (hyper) polarizabilities for some large systems [25]. Fortunately, Champagne et al., have indicated the BHandHLYP method, which is suitable

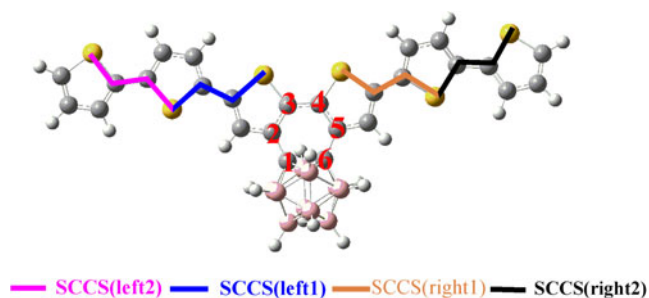


Fig. 2 The table of dihedral angles

for the calculation of the moderate part [26]. Furthermore, Nakano and co-workers pointed out that for a medium-size system, the BHandHLYP method can also reproduce the (hyper)polarizability values from the more sophisticated CCSD(T) method [27]. Obviously, the BHandHLYP method is a good compromise between the quality and efficiency of hyperpolarizability computations. So in this work, the BHandHLYP method was used to explore the dependence of the first hyperpolarizability (β_{tot}), the NBO charge and the most important transitions were calculated at the BHandHLYP/6-31+G*.

The polarizability was defined as follows:

$$\alpha_0 = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \quad (1)$$

The first hyperpolarizability was obtained as

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

where

$$\beta_i = \beta_{iii} + \beta_{ijj} + \beta_{ikk}, \quad i, j, k = x, y, z. \quad (3)$$

All the calculations were performed using the Gaussian 09W program package [28].

Table 1 Geometrical parameters and the bond length alternation (BLA)

Bond	[1, 1]	[1, 2]	[1, 3]	[1, 4]	[1, 5]	[2, 2]	[2, 3]	[2, 4]	[3, 3]
C1–C2	1.486(1.494 ^a)	1.486	1.485	1.485	1.485	1.486	1.486	1.486	1.486
C2–C3	1.386(1.351)	1.387	1.388	1.388	1.388	1.389	1.389	1.389	1.390
C3–C4	1.438(1.419)	1.434	1.434	1.433	1.433	1.431	1.430	1.430	1.429
C4–C5	1.386(1.376)	1.387	1.387	1.387	1.387	1.388	1.389	1.389	1.389
C5–C6	1.486(1.483)	1.486	1.468	1.487	1.486	1.486	1.486	1.486	1.486
C6–C1	1.656(1.634)	1.656	1.655	1.656	1.656	1.656	1.656	1.656	1.656
BLA ^b	0.052	0.047	0.046	0.045	0.045	0.042	0.041	0.041	0.039

^aFor experimental data see ref [24]

^bFor the bond length alternation is calculated between the C2–C4 atoms

Results and discussion

Geometrical parameters

In the present work, the nine molecules are shown in Fig. 1, in which M is the number of thiophene rings on the left part and N is the number of thiophene rings on the right part. For example, the molecule with 1 thiophene ring on the left part and 3 thiophene rings on the right part is labeled as [1, 3]. The number of carbone atoms in center C₆ ring are shown in Fig. 2. Some important parameters of the nine molecules with all real frequencies are shown in Table 1. As one can see from Table 1, the C–C bond lengths of the center C₆ ring are found to be 1.486(C1–C2), 1.386(C2–C3), 1.438(C3–C4), 1.386(C4–C5), 1.4869(C5–C6), 1.656(C6–C1), which are very close to the experimental value of 1.494(C1–C2), 1.351(C2–C3), 1.419(C3–C4), 1.376(C4–C5), 1.483(C5–C6), 1.634(C6–C1). These results show that our computational method used in this work is reasonable. The dihedral angles S–C–C–S of nine molecules are shown in Fig. 2, and the data are listed in Table 2, the results show that there are slightly rotation around the C–C bonds of the thiophenes.

Significantly, the bond length alternation (BLA) is a critical geometrical parameter for a molecules with single and double bonds that governs the amplitude of the NLO responses as it indicates the extent of the delocalization. From Table 1, if we consider the order of [1, 1] > [1, 2] > [1, 3] > [1, 4] > [1, 5] > [2, 2] > [2, 3] > [2, 4] > [3, 3], the BLA value nearly shows the decreased trend. Generally speaking, the smaller BLA value can show better conjugation property which may lead to larger first hyperpolarizability. Does [3, 3] show the largest first hyperpolarizability due to its smallest BLA among these nine molecules?

Static first hyperpolarizabilities

The static first hyperpolarizabilities of the nine molecules are listed in Table 3. It is worth noting that for asymmetric molecules, the major contribution to β_{tot} is β_x , while the greatest contribution to the β_{tot} is β_y for symmetric molecules.

Table 2 The dihedral angles (degree) S-C-C-S (SCCS) of nine molecules

	SCCS(left2)	SCCS(left1)	SCCS(right1)	SCCS(right2)	SCCS(right3)	SCCS(right4)
[1, 1]						
[1, 2]			18			
[1, 3]			12	17		
[1, 4]			11	14	18	
[1, 5]			9	15	13	18
[2, 2]		17	17			
[2, 3]		16	15	17		
[2, 4]		17	16	16	17	
[3, 3]	17	11	11	17		

From Table 3, the result show that the β_{tot} values for symmetric molecules increase with increasing the number of thiophene rings: 39 au of [1, 1] < 66 au of [2, 2] < 903 au of [3, 3], and the orders of β_{tot} values are: 39 of [1, 1] < 800 of [1, 2] < 3553 of [1, 3] < 7998 of [1, 4] < 13049 au of [1, 5] and 66 of [2, 2] < 3240 of [2, 3] < 8029 au of [2, 4]. On the other hand, for molecules with same number of thiophene rings (sum of M and N is constant), larger difference between M and N is, larger β_{tot} values is: 800 au of [2, 2] < 3553 au of [1, 3]; 3240 au of [2, 3] < 7998 au of [1, 4]; 903 au of [3, 3] < 8029 au of [2, 4] < 13049 au of [1, 5] (See Fig. 3). Significantly, the [3, 3], [2, 4] and [1, 5] with six thiophene rings are chosen as example, we found that asymmetric [1, 5] has the largest β_{tot} values to be 13049 au, which is larger than 8029 au of [2, 4], especially greatly larger than 903 au of symmetric [3, 3]. Otherwise, the largest of β_{tot} values of [1, 5] (13049 au) is similar to 1 (encapsulating LiCN \cdots Li from the B-rich edge of BNNT) (17742 au) [29], but larger than the prototypical second-order NLO molecule of *p*-nitroaniline (1679 au) [30].

The nucleus independent chemical shift (NICS), NBO charge population and crucial transition energy (ΔE)

In general, for conjugated cyclic molecules, the aromaticity is a very important property. However, aromaticity cannot be measured directly by experiment. Luckily, some valuable papers show that the nucleus independent chemical shift (NICS) has a strong correlation with aromaticity, which can be calculated by theoretical methods [31, 32]. To obtain further insight into the aromaticity, the NICS values were calculated at the BHandHLYP/6-

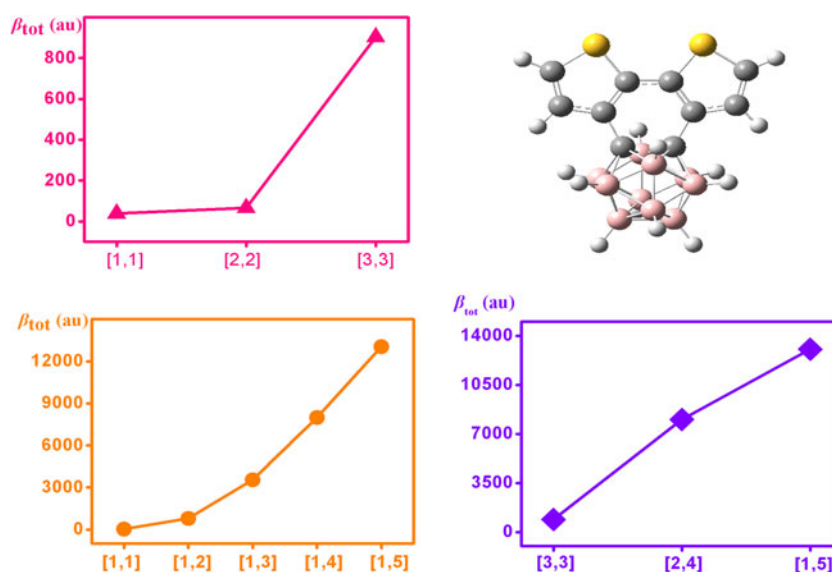
31+G*. As shown in Table 4, the NICS values of the nine molecules are similar, which indicates that increasing the number of thiophene rings has little influence on the NICS values.

Furthermore, the detailed NBO charge population are shown in Table 4 and the NBO charge of thiophene rings on the left labeled as q_1 , the right part labeled as q_2 , the part of carborane labeled as q_3 (see Fig. 4). Would the symmetric and asymmetric configuration influence on the NBO charges? From the results, we can find that increasing or decreasing the number of thiophene rings little influence on NBO charges. As one can see, the q_3 of [1, 1] is -0.170 , and that of [1, 5] is -0.167 . Interestingly, the NBO values of symmetric configuration change little compared with those of asymmetric configuration. For example, when the total number of thiophene rings is 6, the q_3 of [3, 3], [2, 4] and [1, 5] are -0.168 , -0.166 and -0.167 , respectively. And, for the symmetric configuration, the NBO charge of q_1 and q_2 are almost the same: [1, 1] is 0.85, [2, 2] is 0.81, [3, 3] is 0.84, in other words, the symmetry/asymmetry of configuration little influence on the NBO charge.

To gain an understanding of the origin of β_{tot} values, the oscillator strength (f_0) and transition energy (ΔE) were calculated by BHandHLYP/6-31+G*. According to two-level model [33–35], f_0 is proportional to the first hyperpolarizability and the third power of ΔE is inversely proportional to the first hyperpolarizability. As shown in Table 4, for nine molecules, the order of (ΔE) values is 6.094 eV of [1, 1] > 5.365 of [2, 2] > 5.289 of [3, 3] > 3.394 of [1, 2] > 3.032 of [1, 3] > 2.813 of [2, 3] > 2.811 of [1, 4] > 2.677 of [2, 4] > 2.666 of [1, 5]. It is obvious that the order of ΔE values is opposite to that of β_{tot}

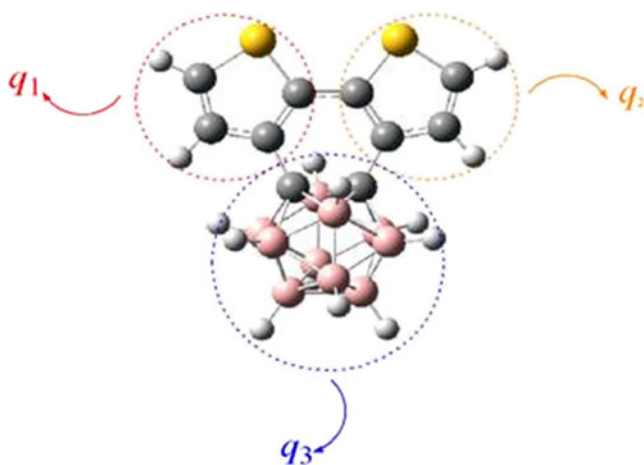
Table 3 The first hyperpolarizabilities β_{tot} (au) of nine molecules

	[1, 1]	[1, 2]	[1, 3]	[1, 4]	[1, 5]	[2, 2]	[2, 3]	[2, 4]	[3, 3]
β_x	1	796	3461	7676	12,776	-0.1	3214	7930	0.2
β_y	-39	82	769	1852	2641	-66	410	1223	903
β_z	0.8	-12	245	-157	-286	-7	54	288	-0
β_{tot}	39	800	3553	7998	13049	66	3240	8029	903

Fig. 3 The structure and first hyperpolarizability**Table 4** Natural bond orbital (NBO) charges, the nucleus independent chemical shift (NICS), oscillator strength (f_0) and transition energy ΔE (eV)

	[1, 1]	[1, 2]	[1, 3]	[1, 4]	[1, 5]	[2, 2]	[2, 3]	[2, 4]	[3, 3]
q_1	0.085	0.084	0.082	0.082	0.083	0.081	0.081	0.082	0.084
q_2	0.085	0.085	0.086	0.086	0.084	0.081	0.083	0.084	0.084
q_3	-0.170	-0.169	-0.168	-0.168	-0.167	-0.162	-0.164	-0.166	-0.168
NICS(0)	-1.2(-1.2 ^a)	-1.5	-1.6	-1.8	-1.5	-1.7	-1.8	-2.1	-2.0
f_0	0.284	0.670	1.128	1.581	2.014	0.363	1.408	1.841	0.324
ΔE	6.094	3.394	3.032	2.812	2.666	5.365	2.813	2.677	5.289

^a For experimental data see ref [24]

**Fig. 4** The definition of NBO charges

values, which is in accordance with the two-level expression. Thus, the variation of β_{tot} for the nine molecules can be explained by ΔE .

As mentioned above, [3, 3] should show larger first hyperpolarizability due to smaller BLA. However, the β_{tot} of [3, 3] is only 903 au, which is far less than that of [1, 5]. It indicates that the influence of BLA on β_{tot} is smaller than that of asymmetric configuration on β_{tot} . Thus, asymmetric configuration is favorable to obtain larger first hyperpolarizability.

Conclusions

In this work, on the basis of three symmetric molecules ([1, 1], [2, 2] and [3, 3]) synthesized by the experiment, we theoretically designed six asymmetric molecules to investigate effect of asymmetric configuration and symmetric configuration on the static first hyperpolarizability. Our results

show that when $M=N$, the β_{tot} values were increased with increasing of M . Interestingly, we found that when the sum of M and N is constant, the larger the difference between M and N , the larger the β_{tot} value. Especially, when the total number of thiophene rings is 4, β_{tot} (3553 au) of the asymmetric configuration [1, 3] is 54 times larger than that (66 au) of the symmetric configuration [2, 2]. Significantly, the order of ΔE values is opposite to that of β_{tot} values, which is in accordance with the two-level expression. This work may encourage a greater focus on designing new thiophene-fused benzocarborane with large NLO responses. And, it is our expectation that this work may have potential to advance the development of new types of NLO materials based on molecules of thiophene-fused benzocarborane.

Acknowledgments The authors gratefully acknowledge financial support from National Nature Science Foundation of China (NSFC 20971020 and 21003019), 973 Program (2009CB623605), Scientific Research Foundation for the Returned Overseas Chinese scholars (SRF for ROCS), State Education Ministry (SEM), Doctoral Fund of Ministry of Education of China (20100043120006), and the Science and Technology Development Planning of Jilin Province (20100178 and 201201062).

References

- Eaton DF (1991) Nonlinear optical materials. *Science* 253:281–287
- Kanis DR, Ratner MA, Marks TJ (1994) Design and construction of molecular assemblies with large second-order nonlinearities. *Quantum chemical aspects*. *Chem Rev* 94:195–242
- Rowley JD, Pierce JK, Brant AT, Halliburton LE, Giles NC, Schunemann PG, Bristow AD (2012) Broadband terahertz pulse emission from ZnGeP_2 . *Opt Lett* 37:788–790
- Nakano M, Kishi R, Ohta S, Takahashi H, Kubo T, Kamada K, Ohta K, Botek E, Champagne B (2007) Relationship between third-order nonlinear optical properties and magnetic interactions in open-shell systems: a new paradigm for nonlinear optics. *Phys Rev Lett* 99:033001
- Plaquet A, Champagne B, Castet F, Ducasse L, Bogdan E, Rodriguez V, Pozzo JL (2009) Theoretical investigation of the dynamic first hyperpolarizability of DHA-VHF molecular switches. *New J Chem* 33:1349–1356
- Zhong RL, Zhang J, Muhammad S, Hu YY, Xu HL, Su ZM (2011) Boron/Nitrogen substitution of the central carbon atoms of the biphenalenyl diradical π dimer: a novel 2e–12c bond and large NLO responses. *Chem Eur J* 17:11773–11779
- Avramopoulos A, Reis H, Li J, Papadopoulos MG (2004) The dipole moment, polarizabilities, and first hyperpolarizabilities of HArF. A computational and comparative study. *J Am Chem Soc* 126:6179–6184
- Chung I, Jang JI, Malliakas CD, Ketterson JB, Kanatzidis MG (2009) Strongly nonlinear optical glass fibers from noncentrosymmetric phase-change chalcogenide materials. *J Am Chem Soc* 132:384–389
- Kirtman B, Champagne B, Bishop DM (2000) Electric field simulation of substituents in donor-acceptor polyenes: a comparison with ab initio predictions for dipole moments, polarizabilities, and hyperpolarizabilities. *J Am Chem Soc* 122:8007–8012
- Muhammad S, Janjua MRSA, Su ZM (2009) Investigation of dibenzoboroles having π -electrons: toward a new type of two-dimensional NLO molecular switch? *J Phys Chem C* 113:12551–12557
- Bredas JL, Adant C, Tackx P, Persoons A, Pierce BM (1994) Third-order nonlinear optical response in organic materials: theoretical and experimental aspects. *Chem Rev* 94:243–278
- Xu HL, Li ZR, Su ZM, Muhammad S, Gu FL, Harigaya K (2009) Knot-isomers of Möbius cyclacene: how does the number of knots influence the structure and first hyperpolarizability? *J Phys Chem C* 113:15380–15383
- Xu HL, Li ZR, Wang FF, Wu D, Harigaya K, Gu FL (2008) What is the shape effect on the (hyper)polarizabilities? A comparison study on the Möbius, normal cyclacene, and linear nitrogen-substituted strip polyacenes. *Chem Phys Lett* 454:323–326
- Blanchard-Desce M, Alain V, Bedworth PV, Marder SR, Fort A, Runser C, Barzoukas M, Lebus S, Wortmann R (1997) Large quadratic hyperpolarizabilities with donor–acceptor polyenes exhibiting optimum bond length alternation: correlation between structure and hyperpolarizability. *Chem Eur J* 3:1091–1104
- Coe BJ, Jones LA, Harris JA, Brunschwig BS, Asselberghs I, Clays K, Persoons A (2002) Highly unusual effects of π -conjugation extension on the molecular linear and quadratic nonlinear optical properties of ruthenium(II) ammine complexes. *J Am Chem Soc* 125:862–863
- Pandey L, Doiron C, Sears JS, Bredas JL (2012) Lowest excited states and optical absorption spectra of donor–acceptor copolymers for organic photovoltaics: a new picture emerging from tuned long-range corrected density functionals. *Phys Chem Chem Phys* 14:14243–14248
- Pal MK, Jain VK, Wadawale AP, Glazun SA, Starikova ZA, Bregadze VI (2012) Synthesis and spectroscopy of cis-configured mononuclear palladium(II) and platinum(II) complexes of chalcogeno o-carboranes and structures of $[\text{Pt}(\text{SCb}^{\circ}\text{Ph})_2(\text{dppm})]$, $[\text{Pt}(\text{SeCb}^{\circ}\text{Ph})_2(\text{dppm})]$, $[\text{Pt}(\text{SCb}^{\circ}\text{S})(\text{PMe}_2\text{Ph})_2]$ and $[\text{Pt}(\text{SCb}^{\circ}\text{S})(\text{PMePh}_2)_2]$. *J Org Chem* 69:4257–4263
- Gruner B, Holub J, Plesek J, Stibr B, Thornton-Pett M, Kennedy JD (2007) Dimethylsulfide-dicarborane chemistry. Isolation and characterisation of isomers [9-(SMe_2)-nido-7, 8- $\text{C}_2\text{B}_9\text{H}_{10}$ -X-Me] (where X = 1, 2, 3 and 4) and some related compounds. An unusual skeletal rearrangement. *Dal Trans* 42:4859–4865
- Morin JF, Sasaki T, Shirai Y, Guerrero JM, Tour JM (2007) Synthetic routes toward carborane-wheeled nanocars. *J Org Chem* 72:9481–9490
- Villagómez CJ, Sasaki T, Tour JM, Grill L (2010) Bottom-up assembly of molecular wagons on a surface. *J Am Chem Soc* 132:16848–16854
- Lamrani M, Hamasaki R, Mitsuishi M, Miyashita T, Yamamoto Y (2000) Carborane-fullerene hybrids as a seemingly attractive-attractive dyad with high hyperpolarizability. *Chem Commun* 17:1595–1596
- Tsuboya N, Lamrani M, Hamasaki R, Ito M, Mitsuishi M, Miyashita T, Yamamoto Y (2002) Nonlinear optical properties of novel carborane-ferrocene conjugated dyads. Electron-withdrawing characteristics of carboranes. *J Mater Chem* 12:2701–2705
- Liu Y, Yang GC, Sun SL, Su ZM (2012) Theoretical investigation on two-dimensional molecule-based second-order nonlinear optical materials of the disubstituted o-carborane derivatives. *Comput Theor Chem* 992:142–149
- Morisaki Y, Tominaga M, Chujo Y (2012) Synthesis and properties of thiophene-fused benzocarborane. *Chem Eur J* 18:11251–11257
- Champagne B, Perpète EA, Jacquemin D, van Gisbergen SJA, Baerends E-J, Soubra-Ghaoui C, Robins KA, Kirtman B (2000) Assessment of conventional density functional schemes for computing the dipole moment and (hyper)polarizabilities of push–pull π -conjugated systems†. *J Phys Chem A* 104:4755–4763
- Champagne B, Botek E, Nakano M, Nitta T, Yamaguchi K (2005) Basis set and electron correlation effects on the polarizability and

- second hyperpolarizability of model open-shell π -conjugated systems. *J Chem Phys* 122:114315–114327
27. Nakano M, Kishi R, Nitta T, Kubo T, Nakasuji K, Kamada K, Ohta K, Champagne B, Botek E, Yamaguchi K (2005) Second hyperpolarizability (γ) of singlet diradical system: dependence of γ on the diradical character. *J Phys Chem A* 109:885–891
 28. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA, Jr., Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2009) Gaussian 09 Revision A.02. Gaussian Inc, Wallingford, CT
 29. Zhong RL, Xu HL, Muhammad S, Zhang J, Su ZM (2012) The stability and nonlinear optical properties: encapsulation of an excess electron compound $\text{LiC}_{60}^{-}\text{Li}$ within boron nitride nanotubes. *J Mater Chem* 22:2196–2202
 30. Kaatz P, Donley EA, Shelton DP (1998) A comparison of molecular hyperpolarizabilities from gas and liquid phase measurements. *J Chem Phys* 108:849–857
 31. Chen Z, Wannere CS, Corminboeuf C, Puchta R, Pvr S (2005) Nucleus-independent chemical shifts (NICS) as an aromaticity criterion. *Chem Rev* 105:3842–3888
 32. Miyake H, Sasamori T, Wu JIC, Schleyer PVR, Tokitoh N (2012) The 4,5,6-triphospha[3]radialene dianion: a phosphorus analogue of the deltate dianion. A NICS (0)(π zz) examination of their aromaticity. *Chem Commun* 48:11440–11442
 33. Datta A, Pati SK (2006) Dipolar interactions and hydrogen bonding in supramolecular aggregates: understanding cooperative phenomena for 1st hyperpolarizability. *Chem Soc Rev* 35:1305–1323
 34. Oudar JL (1977) Optical nonlinearities of conjugated molecules. Stilbene derivatives and highly polar aromatic compounds. *J Chem Phys* 67:446–457
 35. Oudar JL, Chemla DS (1977) Hyperpolarizabilities of the nitroanilines and their relations to the excited state dipole moment. *J Chem Phys* 66:2664–2668