

A new scheme for significant enhancement of the second order nonlinear optical response from molecules to ordered aggregates†

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Weiqli Li,^a Xin Zhou,^b Wei Quan Tian^{*b} and Xiudong Sun^{*a}

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How to achieve maximum nonlinear optical (NLO) properties from the molecular to the macro block is very crucial to the development of nonlinear optical materials, which is the impetus of the present work. Buckybowls present large first hyperpolarizability ascribed to noncentrosymmetric charge distribution due to the curved shape of the system. The role of their packing pattern in maximizing the NLO response of bucky bowl aggregates is investigated. In (corannulene)₁₀ and (sumanene)₁₀ aggregates, the first order hyperpolarizabilities (β_0) per molecule are enhanced 5.59 and 6.21 times with respect to a single entity respectively. For a larger bucky bowl, C₃₆H₁₂, the β_0 value per molecule of its pentamer reaches 191.4×10^{-30} esu which is much higher than conventional dipolar or octupolar NLO chromophores ones. The cohesive coupling among electric dipoles in packing of buckybowls is responsible for significant enhancement of the nonlinear optical response of the aggregates, which could pave the way for designing large 2nd order NLO materials with a good balance of nonlinearity, transparency, and stability.

Introduction

With the development of photonic and optoelectronic devices, numerous experimental and theoretical investigations aimed to characterize the nonlinear optical (NLO) response of organic materials with large π electron systems due to their extremely high optical nonlinearities, wide range of response wavelengths, and short response time.^{1–4} In the past decades, many efforts have been devoted to development of linear molecules with an electron donor (D) and an acceptor (A) connected by a π conjugation bridge, dendrimer and octupolar systems as well.

Such D- π -A compounds exhibit large second order nonlinear optical property which can be tailored with the length of the conjugated π system and strength of the donor and/or the acceptor.^{5,6} One serious shortcoming of this kind of molecule is that the anti-parallel dipole arrangement of molecules in bulk causes the second order macroscopic nonlinear coefficient of material to be zero. Recently, some planar octupolar molecules have been observed to show some advantages to be NLO chromophores, such as possessing large off-diagonal tensor components, vanishing dipole anti-parallel aggregates, and improved efficiency–transparency trade-off.^{7,8} However, the absence of a dipole moment precludes electric field coupling and the application of standard electric field poling techniques. Therefore, the macroscopic packing of octupolar molecules in a noncentrosymmetric environment is a challenge in preparation of nonlinear optical materials.

Carbon-based nanomaterials, represented by graphite, fullerene, and carbon nanotubes, have been extensively explored in the optic-electric field because of their extended delocalized π electron distribution and rigid skeleton. Their first hyperpolarizability tends to be zero or very small due to the symmetrical molecular structure. Some doped fullerenes, defected nanotubes/graphene and various substituted derivatives were designed to increase their quadratic response properties.^{9,10}

Buckybowls, constituted of fullerene fragments, are considered to be another group of key materials whose structures lie between planar and spherical carbon network nanomaterials. They retain the structural stability of fullerenes while presenting some distinctive electronic structure and physical properties:^{11–13} (I) compared with fullerenes, buckybowls present a noncentrosymmetric structure and the curvature of bucky bowl triggers separation of charges in the molecule. Thus, the bucky bowl can be viewed as a large three dimensional dipole. Noncentrosymmetric distribution of π electrons on the bucky bowl surface may generate charge-transfer excited states upon photoradiation, and produce a large nonlinear optical response. (II) Molecular curvature and electronic structure of buckybowls can be adjusted by extension of π conjugated systems and introduction of

^a Department of Physics, Harbin Institute of Technology, Harbin, 150001, China.
E-mail: tccliweiqli@hit.edu.cn

^b State Key Laboratory of Urban Water Resource and Environment, Institute of Theoretical and Simulation Chemistry, Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin, 150001, China.
E-mail: tianwq@hit.edu.cn

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substituents at the edge of buckybowls. (III) The stacking pattern of bowl-shaped molecules in a concave-convex fashion favors formation of a one dimensional column in the molecular dipole direction. Such arrangements have been observed in crystals of sumanene, corannulene, and other buckybowls.^{14–16} These features imply that buckybowls may be a good NLO candidate. Experimental syntheses of buckybowls enable extensive exploration and exploitation of these new nano-materials. In the present work, the electronic structure and NLO properties of some buckybowls will be investigated with first principles calculations.

Computational details

The structures of buckybowls are shown in Fig. 1. The structures of all investigated compounds were optimized at the B3LYP level^{17,18} with the 6–31 + G(d,p) basis set.^{19–22} The stacking pattern and initial structures used for calculation were obtained from reported X-ray experiments.^{14–16} The transition energies (E) and transition dipole moments (M) were calculated with the configuration interaction single excitation within the ZINDO program,²³ and the NLO properties were predicted with the sum of over states (SOS) model.^{24–26} For the first hyperpolarizability, the SOS formula can be written as:²⁵

$$\beta_{ijk} = \frac{1}{4\hbar^2} p(i, j, k; -\omega_\sigma, \omega_1, \omega_2) \times \sum_{m \neq g} \sum_{n \neq g} \left[\frac{\langle g | \mu_i | m \rangle \langle m | \mu_j^* | n \rangle \langle n | \mu_k | g \rangle}{(\omega_{mg} - \omega_\sigma - i\Gamma_{mg})(\omega_{ng} - \omega_1 - i\Gamma_{ng})} \right]$$

Here, $\hbar\omega_{mg}$ is the transition energy from the ground state to the excited state. $\langle g | \mu_i | m \rangle$ are electronic transition moments between the unperturbed ground state and the excited state. $\langle m | \mu_j^* | n \rangle$ denotes the dipole differences between the ground state and the m th excited state when m and n are the same excited state. ω_1 and ω_2 are frequencies of radiation fields and $\omega_\sigma = \omega_1 + \omega_2$ with ω_σ being the polarization response frequency.

Results and discussion

The important structural parameters, absorption spectra and the first hyperpolarizabilities of all investigated molecules are listed in Table 1. The π -orbital axis vector (POAV) method proposed by Haddon is applied to describe carbon surfaces curvature.²⁷ The π -orbital axis vector is defined to make it equal-angled ($\theta_{\sigma\pi}$) to the three σ -bonds at a conjugated carbon atom, and the pyramidalization angle is obtained as $\theta_P = (\theta_{\sigma\pi} - 90^\circ)$, which measures the variance of the planarity of the sp^2 hybridized carbon. As the size of the bowl increases, pyramidalization angles of carbon atoms at the core (θ_P) and the average ones (θ_P^{av}) of all carbon atoms with no hydrogen attached increase rapidly. Variation of the molecular dipole moment is roughly proportional to the size of molecules. The dipole moment of two deep buckybowls, $C_{40}H_{10}$ and $C_{39}H_{12}$, reaches 6.0 D, which is close to that of conventional D– π –A molecules.

The first hyperpolarizabilities of buckybowls have the following features:

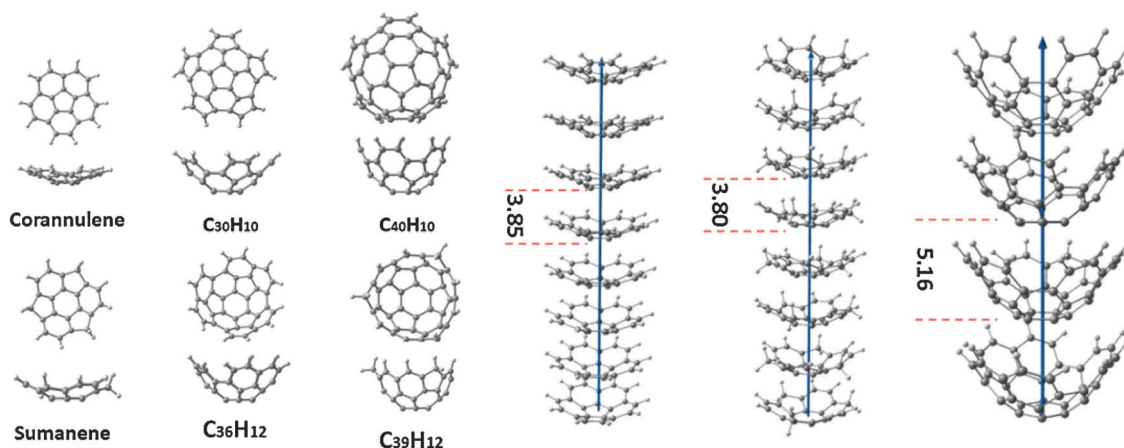


Fig. 1 Molecular structures of investigated buckybowls and their crystal packing pattern (arrows represent the direction of dipole moments of aggregates).

Table 1 Molecular π -orbital axis vector (θ , in degree) and dipole moments (predicted by ZINDO, in debye), static first hyperpolarizabilities, corresponding dipolar and octupolar components (in $10^{-30} \text{ cm}^5 \text{ esu}^{-1}$), and the maximum absorption wavelengths (λ_{max} in nm)

Compound	θ_P	θ_P^{av}	λ_{max}	μ	β_{ZZZ}	β_{ZXX}	β_{ZYY}	$ \beta_{J=1} ^2$	$ \beta_{J=3} ^2$	$ \beta_0 ^2$
$C_{20}H_{10}$	8.12	5.91	317.2	1.96	0.95	3.50	3.50	6.18	6.08	8.67
$C_{30}H_{10}$	12.4	8.91	432.5	4.34	8.32	12.70	12.70	26.10	18.80	32.10
$C_{40}H_{10}$	12.2	10.16	437.5	5.45	23.6	15.20	15.20	41.90	13.90	44.10
$C_{21}H_{12}$	8.90	6.90	375.0	2.85	1.21	3.30	3.30	6.06	5.50	8.18
$C_{36}H_{12}$	12.0	8.20	422.4	5.40	16.31	13.20	13.20	33.10	14.70	36.20
$C_{39}H_{12}$	12.20	11.30	450.8	6.02	25.6	16.6	16.5	45.5	15.2	48.0

(I) Three dimensional charge transfer induced by noncentrosymmetric molecular structures results in large off-diagonal β tensor components. In the case of shallow buckybowl, their β_{ZX} and β_{ZY} are larger than the dipole tensor component, β_{ZZ} . However, ratios of off-diagonal β tensor components *versus* diagonal ones become smaller as the molecular dipole moment of deep buckybowl increases. The large off-diagonal tensor can ensure that the second harmonic response does not depend on the polarization of the incident light.²⁸

(II) For buckybowl, compared with the linear dipolar molecule and planar octupolar molecules, more charge transfer channels can form for transition from ground state to excited states. Some transition dipoles lie in the (x,y) direction with small transition energies and large oscillator strengths, and associate with doubly degenerate excited states. Other transition dipoles lie in the molecular dipole direction with large transition moment. They produce a large dipole difference between the ground state and the excited state, and require relatively high transition energy. Thus, in the framework of the SOS perturbation theory, both contributions, $\beta(2 \text{ level})$ and $\beta(3 \text{ level})$, are important to the first hyperpolarizability of buckybowl compounds. $\beta(J=1)$ dipolar contributions and $\beta(J=3)$ octupolar contributions to molecular hyperpolarizability were calculated by the method proposed by Zyss and Ledoux.²⁹ For conventional dipolar molecules and planar octupolar molecules, the first hyperpolarizabilities are dominated by dipolar and octupolar components respectively. For buckybowl, both dipolar and octupolar components contribute significantly to the first hyperpolarizabilities. As the size of buckybowl increases, the contributions of both components increase, and dipolar contribution becomes dominant in the first hyperpolarizability of deep buckybowl.

(III) Similar to fullerenes, the π conjugation of carbon atoms is weakened due to large molecular curvature.³⁰ The maximum absorption peak of buckybowl appears in the near-ultraviolet region in the range from 280 to 460 nm. This indicates the superiority of the buckybowl over conventional linear chromophores in terms of optical nonlinearity without significant loss of transparency, and it needs to be taken into account in practical applications.

(IV) The present predictions show that the buckybowl is one of a few pure hydrocarbon compounds with a large nonlinear optical response. Its static average β values are comparable to

those of *p*-nitroaniline (PNA), $\beta_0 = 12.0 \times 10^{-30}$ esu, and 1,3,5-triamino-2,4,6-trinitrobenzene, $\beta_0 = 22.0 \times 10^{-30}$ esu,⁸ and exhibits the same order of magnitude as those of dimethylaminonitrostilbene (42.1×10^{-30} esu)³¹ and 1,3,5-tricyano-2,4,6-tris(vinyl)benzene (63×10^{-30} esu)³² which are considered to be the most representative linear and planar octupolar NLO molecules. The substituent effect could further enhance the NLO properties^{31,33} and this effect is not considered for buckybowl in the present work. It is well known that curved carbon nanomolecules are good electron acceptors, and introduction of strong donors could enhance the first hyperpolarizability of buckybowl significantly. Therefore, from the perspective of molecular stability and optical properties, buckybowl could serve as excellent NLO chromophore candidates.

Orientation of NLO chromophores, intermolecular interaction, crystal oxidation/reduced state, and the molecular packing style in assembling thin films or crystal have important effects on the NLO properties of materials.³⁴ Recent reports revealed that NLO chromophores distributed in some dipolar dendrimers or octupolar dendrimers in a semi-rigid noncentrosymmetric manner can keep macromolecules with an electronically dipolar structure. Their β per unit are significantly enhanced by strong coupling between molecular units.^{35,36} Crystals of buckybowl present one dimensional column structures in the molecular dipolar direction, and the distance between adjacent bowls is similar to that between graphene layers. Accurate calculation indicated that intermolecular interaction in crystals of buckybowl is much larger than that in graphene.^{37,38} In this packing pattern, intermolecular dipole-dipole interaction (as shown in Fig. 1) is the main force that maintains the ordered arrangement of buckybowl in crystals. This fascinating crystal structures are expected to bring about distinctive physical properties. Recent work demonstrated large anisotropic conductivity of single crystals of sumanene.¹⁶ Enhanced optical properties of buckybowl crystals are also expected due to the external field-induced charge transfer because the mechanism for enhanced optical properties is similar to that of conduction.

The molecular hyperpolarizability in multi-component systems can be estimated with the cluster model in which the effective molecular hyperpolarizability of the multi-component system is the sum of the contribution of each chromophore. As shown in Fig. 2, the dipole moment of aggregates exhibits a good linear relation to the number of molecular units in the aggregates,

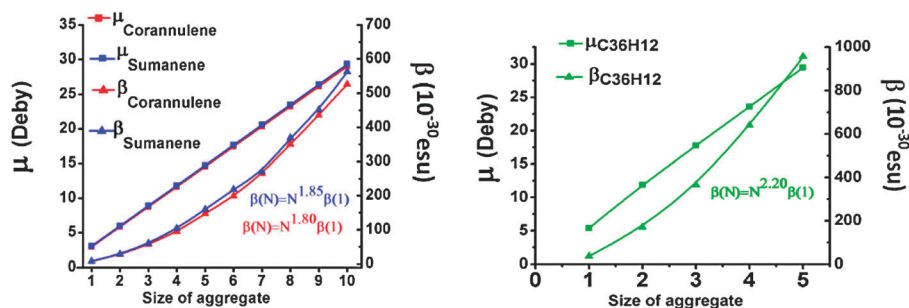


Fig. 2 Evolution of dipole moments and the first hyperpolarizability with the number of molecular units in aggregates.

while the β_0 of aggregates exponentially increases with the number of molecules in aggregates and it can be expressed by the formula $\beta_0(N) = N^P \beta_0(1)$, with N being the number of molecular units in aggregates. The exponential values are 1.80, 1.85, and 2.20 for $C_{20}H_{10}$, $C_{21}H_{12}$, and $C_{36}H_{12}$ crystals, respectively. In the case of dimers of corannulene, sumanene, and $C_{36}H_{12}$, the first hyperpolarizabilities per unit are 1.71, 1.79, and 2.36 times larger than that of the corresponding monomer. When the number of units in corannulene and sumanene aggregates reaches 10, the β_0 values per unit are 52.6×10^{-30} esu and 56.3×10^{-30} esu, approximately 5.59 and 6.20 times larger than those of the corresponding monomers respectively. For the pentamer of $C_{36}H_{12}$, the β_0 per unit reaches 191.4×10^{-30} esu, 5.28 times larger than that of the monomer. Compared with buckybowl aggregates, the first hyperpolarizability of an azobenzene dendrimer with 15 chromophoric units is 1.34 times larger than the sum of 15 isolated azobenzene monomers.³⁵ For the three buckybowls, the maximum absorptions of their aggregates are nearly identical to the corresponding monomer, thus high transparency of material is expected in bulk.

The increase of the first hyperpolarizability of the stacking aggregates could be rationalized based on the properties of some important excited states of aggregates. Firstly, due to the interaction among monomers, the number of excited states increases as shown in Fig. 3, providing more effective electronic coupling channels between ground and excited states. Secondly, ordered arrangement of buckybowls along the molecular dipole direction leads to a macro-dipole moment in aggregates. The buckybowl is placed in a large electric dipole field created by the other buckybowls in aggregates, thus the π electrons on the buckybowl are even more susceptible to the external electric field. The oscillator strength of charge-transfer (CT) transitions is enhanced significantly. As illustrated in Fig. 3, some characteristic absorption peaks are maintained from monomers to aggregates, yet their oscillator strengths increase dramatically with respect to those in their corresponding monomers. In the case of absorption spectra of a sumanene tetramer, a blue-shift of 8.0 nm occurs for the strongest absorption peak as compared to the monomer, and the oscillator strength is nearly twice as much as that of the monomer. Thirdly, cross-excitation with intermolecular CT transition is an important feature of the spectra of aggregates. In the case of the maximum absorption wavelength, the oscillator strengths of

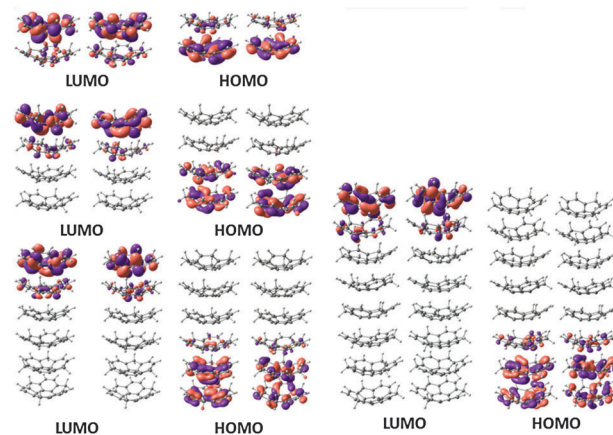


Fig. 4 The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of (sumanene)_n ($n = 2, 4, 6, 8$).

aggregates are 3.7, 7.2, 14.3, and 17.3 times enhanced in the dimer, tetramer, hexamer, and octamer of sumanene with respect to that of the monomer as shown in Table S2 (ESI†). Related main molecular orbitals in the first excited state, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), are shown in Fig. 4. Electron density is localized at the bottom and top of buckybowl aggregates in the HOMO and LUMO respectively. Those orbitals manifest the intermolecular CT mechanism in the first excited state of buckybowl aggregates. Similar controlled photoelectric properties by intermolecular CT were also reported.³⁹ All intermolecular CT transitions in aggregates have very a strong transition dipole moment along the dipole direction and lead to extremely large dipole moment fluctuation ($\Delta\mu$) between the ground state and the excited state, which consequently enhances the hyperpolarizabilities of the systems.

The concave-convex longitudinal stacking of buckybowls along their dipole direction in buckybowl crystals leads to longitudinal dipole interaction among buckybowls and charge redistribution, thus amplifying the second order NLO coefficients of materials. Based on such stacking patterns, further enhancement of the second nonlinear optical coefficient of materials could be achieved by tuning of molecular structure, such as increasing the depth or size of buckybowls, and introduction of functional groups into peripheral carbon atoms of buckybowls,

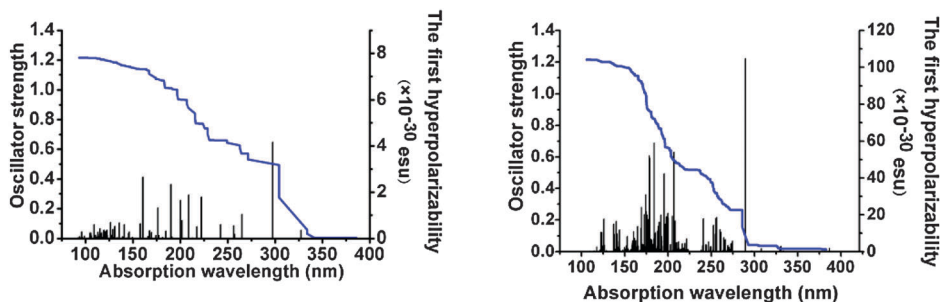


Fig. 3 The ZINDO/SCI predicted electronic spectra and the average of the first hyperpolarizabilities of the monomer (β , left) and the tetramer (β , right) of sumanene.

which can essentially enhance the dipole moment of the molecule.

Summary

The structure and optical properties of potential NLO materials, buckybowl, have been investigated with quantum mechanics methods and the SOS model. The buckybowl is significantly curved from planar conjugated compounds. Such curvature interrupts the conjugation of π electrons, shortens the λ_{max} , and in turn enhances the transparency of materials in the visible region for NLO properties. The depth of the buckybowl (which consequently enlarges the dipole moment of the buckybowl) has a significant effect on the 2nd order NLO response (dipole contribution $\beta_{J=1}$ and octupole contribution $\beta_{J=3}$) of the system.

The dipole–dipole coupling among buckybowl stabilizes the concave–convex packing pattern in aggregates with a large dipole along the packing direction, which in turn induces a significantly enhanced 2nd order NLO response. The empirical scaling formula for buckybowl aggregates ($\beta(N)$, N is the number of buckybowl) is $\beta(N = 1) \times N^p$, with p being a constant.

The present work provides a promising route for optimizing nonlinear optical materials with nonlinearity–transparency–stability trade-offs and suggests experimental trials.

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