



Hydrogen-bond-directed-linking solving transparency-efficiency tradeoff in nonlinear optical molecule



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ABSTRACT

It is well known that settling transparency-efficiency tradeoff is important to design nonlinear optical (NLO) materials. In this work, we constructed one-dimensional polymeric cyanoacetylene ($\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$)_n by hydrogen-bond-directed-linking to understand this tradeoff from molecular level. Results show that the first hyperpolarizability of ($\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$)_n ($n=2-8$) gradually increased with the increase of n , and what is more important is that the red-shifts, associated with the increase of n , were very little. It is proposed that these polymeric structures possess double-degenerated charge transitions, which contribute to the hyperpolarizability in an additive fashion, and that the coupled oscillators are gradually improved, which lead to the increase of the first hyperpolarizability. Therefore, we propose the hydrogen-bond-directed-linking idea is helpful to develop the potential high-performance NLO materials.

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1. Introduction

The study of the NLO properties of organic compounds in theory and experiment [1–14], is an issue of great research interest due to their broad potential application in telecommunications, information storage, optical switching and signal processing which depends on the development of high-performance NLO materials to a large degree.

One-dimensional push–pull chromophores with π -conjugated systems end-capped by donor (D) and acceptor (A) moieties are particularly promising NLO materials [15–18], because they can exhibit modulated molecular hyperpolarizability β by optimizing donor/acceptor moiety strengths and/or extending π -conjugated path. However, one-dimensional structural compounds present some drawbacks in some areas, such as, the transparency-efficiency tradeoff [19,20], the phase matching conditions [21,22], and the formation of a centrosymmetric arrangement. Here, what we concerned most is the transparency-efficiency tradeoff. According to the two-level model of Oudar and Chemla [23], the static first hyperpolarizability β_0 is proportional to oscillator

strength for the single transition multiplied by the third power of the absorption maximum λ_{max}^3 , and in generally, the λ_{max} is an approximate measure of the transparency achievable in NLO materials. Therefore, the loss of transparency (the red-shift) is unavoidable consequence of any increase in β [24]. Moreover, most one-dimensional D– π –A structural molecules are prone to form the centrosymmetric arrangement in the crystal, due to the dipole–dipole intermolecular interaction, in this way, they exhibit no second harmonic generation (SHG) response. The use of electric field poling and the preparation of Langmuir–Blodgett (LB) thin films were proposed to limit the natural antiparallel dipolar interaction [25]. Besides, significant NLO responses have also been observed in nondipolar octupolar molecules [26,27], because of the lack of a permanent dipole moment contributing to noncentrosymmetric arrangements; A third approach that can rule out of the formation of centrosymmetric arrangement is exploiting Λ -shape molecules, owing to the large off-diagonal β -tensor component [28–30]; another approach involves the preparation of helical/chiral compounds, for example, helical carbon structure [31], carbon–boron–nitride heteronanotubes [32], spiral donor– π –acceptor frameworks based on 4-nitrophenyldiphenylamine [33], which present the advantage of providing a way for positioning peripheral substituents in a well-defined spatial arrangement.

In this work, a new promising hydrogen-bond-directed-linking approach was proposed to understand the transparency-efficiency tradeoff in NLO material design. As we know, many experimental

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and theoretical publications are devoted to investigate hydrogen bonds, which play an essential role in numerous chemical, biochemical, and biological processes [34]. It is usually represented as a form of $\text{XH} \cdots \text{Y}$, where X and Y are electronegative elements or groups. Hydrogen bonds are apparently unique among ion–dipole bonds in that evidence indicates that they are saturable and directional, which can limit the formation of centrosymmetric arrangement. In addition, weak $\text{C-H} \cdots \text{Y}$ hydrogen bonds involving electronegative atoms, anions, or π -systems are important stabilizing forces in crystal engineering and anion recognition in solution [35,36]. Yang et al. investigated that hydrogen bonds between the sulfonic oxygen atoms and double-bond hydrogen atoms play a role in crystal packing and chromophores orientation [37]. Especially, Kwon et al. proposed [38] a configurationally locked polyene (CLP) crystal 2-(3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile (OH1) containing a phenolic electron donor, which also acts as a hydrogen bond donor, which exhibited highly efficient second-harmonic generation at 1907 nm fundamental wavelength. Nagalakshmi et al. [39] calculated that the first hyperpolarizability of single crystals of hydroxyethylammonium L-tartrate monohydrate [HEALT] stabilized by a set of intermolecular hydrogen bonds is found to be 4.238×10^{-30} esu, which is 14.2 times that of urea. Further, Wang et al. calculated first-order hyperpolarizability of L-arginine 4-nitrophenolate 4-nitrophenoldehydrate (LAPP) crystal and β_{tot} is 3.11×10^{-29} esu, which is nearly 116 times that of urea [40]. Although many works have been carried out to investigate the impact of H-bonds on the first hyperpolarizability for hydrogen-bonded π -electronic systems [41,42], the transparency for this kind systems have not been further investigated. Therefore, the hydrogen-bond-directed-linking approach is expected to exploit NLO materials with high transparency.

Cyanoacetylene is a fascinating organic compound with formula $\text{C}_3\text{HN}(\text{N}=\text{C}=\text{C}=\text{H})$, which has been detected by spectroscopic methods in interstellar clouds, in the coma of comet Hale–Bopp and in the atmosphere of Saturn's moon Titan [43]. And cyanoacetylene is also one of the molecules that was produced in the Miller–Urey experiment [44]. This compound has played an important role in the prebiotic synthesis of amino acids and purines or pyrimidines [45]. In this paper, cyanoacetylene is employed to investigate the promising hydrogen-bond-directed-linking approach to design NLO molecule. Since we understand the formation of the hydrogen bond, a number of cyanoacetylene can naturally form one-dimensional polymeric cyanoacetylene ($\text{N}=\text{C}=\text{C}=\text{H})_n$ by hydrogen-bond-directed-linking.

In this paper, we described our studies on one-dimensional polymeric cyanoacetylene ($\text{N}=\text{C}=\text{C}=\text{H})_n$ ($n=2-8$) by hydrogen-bond-directed-linking. Theory calculations showed that their first hyperpolarizabilities increased with the increase of n , and the red-shifts associated with the increase of n are very little. Therefore, ($\text{N}=\text{C}=\text{C}=\text{H})_n$ can exhibit first hyperpolarizability and little red-shift, which is helpful to solve the transparency-efficiency tradeoff. We presented the evidences that the excellent β_0 values are due to the existence of double-degenerated charge transition states, which contribute to β_0 in an additive manner. Thus, by using hydrogen-bond-directed-linking method, we can obtain one-dimensional structure ($\text{N}=\text{C}=\text{C}=\text{H})_n$, exhibiting gradually enhanced first hyperpolarizability with little red-shift.

2. Computational methods

First, considering the dimer ($\text{N}=\text{C}=\text{C}=\text{H})_2$ with different interaction orientation, we found that the linear dimer by hydrogen bond interaction is the most stable one. Thus, in this work, the studied one dimensional structures of ($\text{N}=\text{C}=\text{C}=\text{H})_n$ ($n=2-8$)

can be polymerized by hydrogen-bond-directed-linking. The optimized geometric structures of ($\text{N}=\text{C}=\text{C}=\text{H})_n$ ($n=2-8$) with all real frequencies were obtained through using second-order Møller–Plesset (MP2) theory and the 6-31+G(d) basis set. Natural bond orbital (NBO) [46,47], were carried out at the same level as the geometry optimization to understand the nature of hydrogen bond. The intramolecular interaction energies (E_{int}) between ($\text{N}=\text{C}=\text{C}=\text{H})_1$ and ($\text{N}=\text{C}=\text{C}=\text{H})_{n-1}$ were calculated at the MP2/6-31+G(d) level. We used the counterpoise (CP) [48] procedure to eliminate the basis set superposition error (BSSE) effect given by Eq. (1):

$$E_{\text{int}} = E_{(\text{N}=\text{C}=\text{C}=\text{H})_n}(\text{X}_{(\text{N}=\text{C}=\text{C}=\text{H})_n}) - E_{\text{N}=\text{C}=\text{C}=\text{H}}(\text{X}_{(\text{N}=\text{C}=\text{C}=\text{H})_n}) - E_{(\text{N}=\text{C}=\text{C}=\text{H})_{n-1}}(\text{X}_{(\text{N}=\text{C}=\text{C}=\text{H})_n}) \quad (1)$$

where the same basis set, $\text{X}_{(\text{N}=\text{C}=\text{C}=\text{H})_n}$, was used for the subunit energy ($E_{(\text{N}=\text{C}=\text{C}=\text{H})_1}$ and $E_{(\text{N}=\text{C}=\text{C}=\text{H})_{n-1}}$) calculation as for the energy $E_{(\text{N}=\text{C}=\text{C}=\text{H})_n}$ calculation.

The (hyper)polarizabilities of ($\text{N}=\text{C}=\text{C}=\text{H})_n$ are calculated by MP2 method. First, we have tested the accuracy of MP2 method by comparing with higher level CCSD and QCISD calculations for the case of the monomer $\text{N}=\text{C}=\text{C}=\text{H}$ (see Table S1 in Supplementary material). Second, taking a medium structure ($\text{N}=\text{C}=\text{C}=\text{H})_5$ as an example, a detail discussion about the difference of β values by a systematic extension of basis sets has been given in Table S2. From Tables S1 and S2 in Supplementary material, we found that, considering reliability and computational costs, it is suitable that the MP2/6-31+G(d) level was chosen to calculate first hyperpolarizability. For the calculation of the hyperpolarizability, the finite-field (FF) method is employed, and the magnitude of the applied electric field is chosen to be 0.0010 a.u.

The transition properties of ($\text{N}=\text{C}=\text{C}=\text{H})_n$, including the transition energy ΔE and oscillator strength f_0 , were calculated by the time-dependent density-functional theory (TDDFT) approach using the LC-BLYP [49,50] functionals, which perform well for charge transfer excitations. Besides, the results of TDDFT are compared with those of the configuration interaction singles (CIS) method. The study of Gustavo E. Scuseria et al. shows that CIS results are a useful first approximation and give good qualitative agreement with experiment for the planar conjugated molecule C_6H_6 [51] (see Table S3 in Supplementary material).

In the FF method, when a molecule is subjected to the static electric field, the energy (E) of the molecule is expressed

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

where E^0 is the energy of the molecule in the absence of an electronic field, μ is the component of the dipole moment vector, α is the linear polarizability tensor, β and γ are the first and second hyperpolarizability tensors, respectively, and i, j , and k label the x , y , and z components, respectively.

For a molecule, the average dipole moment (μ_0) and polarizability (α_0) are defined as follows:

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (3)$$

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (4)$$

The static first hyperpolarizability is noted as

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (5)$$

where

$$\beta_i = \frac{3}{5}(\beta_{iii} + \beta_{iji} + \beta_{ikk}), \quad i, j, k = x, y, z$$

All calculations were performed using the GAUSSIAN 09 program package [52].

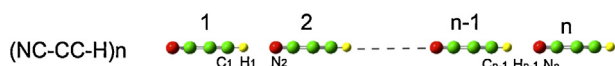
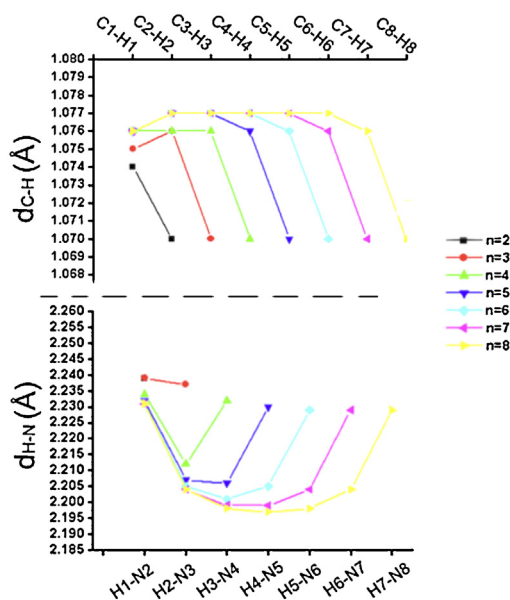


Fig. 1. One-dimensional hydrogen-bond structure.

Fig. 2. The distances of C_n-H_n and H_n-N_{n+1} .

3. Results and discussion

3.1. One-dimensional polymeric cyanoacetylene by hydrogen-bond-directed-linking

A novel hydrogen-bond-directed-linking provides one-dimensional NLO molecular structures $(N\equiv C-C\equiv C-H)_n$ ($n=2-8$) depicted in Fig. 1. Considering the calculation cost at the MP2/6-31+G(d) level, the polymerization number n is up to 8, which is sufficient to illustrate the change rule of structure and first hyperpolarizability with the increase of n .

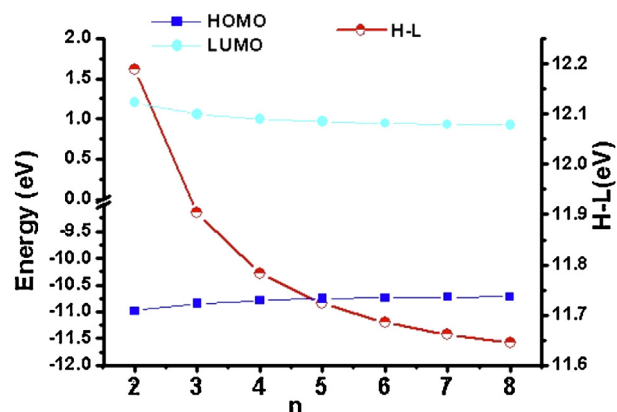
Comparing with traditional hydrogen bond (HB) form $XH\cdots Y$, where X and Y are electronegative elements or groups, there exists a novel π -HB- π interaction in the one-dimensional structures $(N\equiv C-C\equiv C-H)_n$, due to conjugated interaction. Then, the novel π -HB- π interaction leads to the striking changes of the C-H and H-N distances. As shown in Fig. 2, it is obvious that the C-H distances become shorter comparing with that in the monomer $N\equiv C-C\equiv C-H$. The detailed parameter can be found in Table S4 in Supplementary material. The most unexpected changes we observed are: (1) that the H-N distances become shortened with the increase of n , except for the H-N distances in the two ends of one dimensional structures; (2) in every structure, the H-N distances in the middle are shorter than those in two ends, that is say, the H-N distances exhibit a contractile phenomena. Therefore, our observations indicate that the novel π -HB- π interaction is strong; moreover, the interaction would become stronger with the increase of n . The NBO charge analysis is also in line with the above observations (see Table S5 in Supplementary material). As there exist the novel π -HB- π interaction, the change of q_H is insignificant.

The hydrogen bond strength in the fascinating structures $(N\equiv C-C\equiv C-H)_n$ is an important criterion in the evaluation their stabilities. As mentioned above, the H-N distances exhibit a contractile phenomenon that the H-N distances in two ends are longer than those in the middle; especially, the H1-N2 distances are the longest in all hydrogen bond. Thus, the hydrogen bond H1-N2

Table 1

Combined energies E_c (kcal/mol) and HOMO-LUMO energy gaps (eV).

n	E_c	HOMO	LUMO	H-L
2	3.991	-10.983	1.204	12.187
3	4.593	-10.844	1.058	11.902
4	4.756	-10.787	0.995	11.782
5	4.817	-10.757	0.965	11.722
6	4.845	-10.741	0.943	11.684
7	4.860	-10.727	0.932	11.659
8	4.869	-10.719	0.924	11.643

Fig. 3. The relationships between HOMO-LUMO gap and n .

should be the weakest bond for every structure. The most possible rupture zones should be H1-N2 bonds. So, we calculated the combined energies of those bonds to evaluate the stabilities of those structures at the MP2/6-31+G(d) level. In this study, the combined energy (E_c) is defined as the negative of the intramolecular interaction energy between $(N\equiv C-C\equiv C-H)_1$ and $(N\equiv C-C\equiv C-H)_{n-1}$, which is calculated by Eq. (1). As shown in Table 1, $(N\equiv C-C\equiv C-H)_n$ possess the combined energies ranging from 3.99 to 4.87 kcal/mol, which are comparable to those of other moderate hydrogen bonds (~ 4.28 kcal/mol for the dimer $(HF)_2$ [53] and ~ 3.95 kcal/mol for the hydrogen bond complex $H_2CS-HOF$ [54]).

And from Table 1, we can find that the combined energies increased with the increase of n , which gives a hint that the larger the polymerization number n is, the more stable the obtained one dimensional structure become. This also shows that the $(N\equiv C-C\equiv C-H)_n$ which contains more π electrons can form stronger hydrogen bond. Moreover, the HOMO-LUMO energy gap is a useful quantity for examining the stabilities of those structures. From Table 1, the HOMO-LUMO gaps of the $(N\equiv C-C\equiv C-H)_n$ range from 11.644 to 12.188 eV. These gap values are comparable to those of 7.58–10.58 eV for stable superalkali cations OM_3^+ ($M = Li, Na, K$) [55]. Although the gaps decrease with the increase of n , the difference-values become smaller and smaller (see Fig. 3). From Fig. 3, we inferred that the gaps are still greater than 11 eV, even though when n is large enough. Those indicate the high stabilities of those one-dimensional structures.

3.2. Large first hyperpolarizability and little red-shift

Table 2 lists the calculated dipole moments, polarizabilities, and first hyperpolarizabilities of $(N\equiv C-C\equiv C-H)_n$, respectively. Several aspects of the data are conspicuous. First, it is clear that the dipole moments μ of $(N\equiv C-C\equiv C-H)_n$ are quite large. Generally speaking, the magnitude of the dipole moment is determined by the charge distributions in each structure. From Table 2, it is found that the μ values monotonously increase at the steady steps of 6 D with the increase of n . Thus, it suggests that the growth of

Table 2
First hyperpolarizabilities β (a.u.) and their components, polarizabilities α (a.u.), dipole moments μ (Debye), absorptions maximum wavelength λ_{\max} (nm), transition energy ΔE (eV) and oscillator strengths f .

n	β_{xxz}	β_{yyz}	β_{zzz}	β_z	β_0	α	μ	λ_{\max}	ΔE	f
2	−19	−19	264	135	135	72	9.978	147.6	8.399	3.240
3	−27	−27	568	308	308	112	15.909	149.8	8.275	5.256
4	−34	−35	907	502	502	152	21.926	151.4	8.192	7.095
5	−41	−42	1257	704	704	192	27.937	152.3	8.139	8.871
6	−48	−49	1614	910	910	233	34.037	152.9	8.105	10.615
7	−56	−56	1973	1116	1116	273	40.107	153.4	8.080	12.340
8	−63	−64	2335	1324	1324	313	46.182	154.0	8.047	14.148

one-dimensional structures $(\text{N}\equiv\text{C}-\text{C}\equiv\text{H})_n$ strength π effect to contribute the charge distributions. Second, it is found that the polarizabilities α values also monotonously increase at the steady steps of 40 a.u. with the increasement of n . This result is in accordance with the early result that the polarizability depends on the number and kind of elements in the molecule [56].

Third, π -HB- π interactions significantly increase the first hyperpolarizability. Particularly, it is found that the first hyperpolarizabilities of $(\text{N}\equiv\text{C}-\text{C}\equiv\text{H})_n$ ($n=2-8$) gradually increase with the increase of n , which exhibit modulated molecular hyperpolarizability by controlling n . When $n=8$, the β_0 of $(\text{N}\equiv\text{C}-\text{C}\equiv\text{H})_8$ is up to 1324 a.u., which is very close to that of one-dimensional Li@B-BNNT (~ 1350 a.u.) [57] obtained by doping the Li atom to the edge of BNNT. Obviously, this polymeric pattern favors to contribute the increase of β_0 value, which consistent with Su' study [58] where the radical dimerization can effectively enhance the magnitude of third order non-linear optical response. From Table 2, although the β_{xxz} and β_{yyz} components and the β_{zzz} component have opposite signs, the β_{zzz} components are large and responsible for the β_0 , and in contrast, the β_{xxz} and β_{yyz} components are insignificant. We only concerned the changes of β_{xxz} , β_{yyz} and β_{zzz} components to understand the change of β_0 . Those changes are depicted in Fig. 4. From Fig. 4, it is shown that $\Delta\beta_{xxz}$ and $\Delta\beta_{yyz}$ values are small (~ 7 a.u.), while $\Delta\beta_{zzz}$ value is large (up to 360 a.u.). Thus, the β_0 (β_z) values are increased linearly with the increase of n . Comparing with other one-dimensional systems, for the pure ladder-type PDA [59], the β_{zzz} values only have a small rise with the increase of the chain length, its $\Delta\beta_{zzz}$ value is smaller than that for $(\text{N}\equiv\text{C}-\text{C}\equiv\text{H})_n$. However, the $\Delta\beta_{zzz}$ value is much smaller than that for one-dimensional polymer $[\text{Li}^+[\text{calix}[4]\text{pyrrole}][\text{Li}^-]_n$ [60], the contribution of every unit on $\Delta\beta_0$ is up to 19803 a.u. Hence, the β_0 of $(\text{N}\equiv\text{C}-\text{C}\equiv\text{H})_8$ (1324 a.u.) is smaller those of one-dimensional carbon-boron-nitride heteronanotubes systems, for example, the β_0 of BN-1 is 1.05×10^4 a.u. [61], and the β_0 of Li5-BN-1a is 3.22×10^4 a.u. [62]. However, because of $(\text{N}\equiv\text{C}-\text{C}\equiv\text{H})_n$ having large $\Delta\beta_{zzz}$ value, the β_0 of $(\text{N}\equiv\text{C}-\text{C}\equiv\text{H})_n$ would increase with increase of n . We expect the β_0 of $(\text{N}\equiv\text{C}-\text{C}\equiv\text{H})_n$ would

close to those of BN-1 and Li5-BN-1a, when n is up to 35 and 85, respectively.

Fourth, the most important finding is that hydrogen-bond-directed-linking approach is helpful to solve the transparency-efficiency tradeoff. In generally, the absorptions maximum wavelength λ_{\max} is an approximated measure of the transparency achievable in a given chromophore. Unfortunately, it has been shown that the β_0 value is a strong function of λ_{\max} . According to the two-level model of Oudar and chemla [23,63], the static first hyperpolarizability is proportional to oscillator strength for the single transition multiplied by the third power of the absorption maximum λ_{\max}^3 . Therefore, the loss of transparency (the red-shift) is unavoidable consequence of any increase in β . But, as listed in Table 2, when increasing n , the λ_{\max} values only slightly increase. So, one-dimensional $(\text{N}\equiv\text{C}-\text{C}\equiv\text{H})_n$ hugely enhance NLO response without sacrificing much transparency. In practice, for the compounds with good nonlinearity-transparency, people expect that a $\log\beta$ v $\log\lambda_{\max}$ plot would exhibit a greater than normal slope [64,65]. The plots are shown in Fig. 5. From Fig. 5, the slope is approximately 59, a substantial increase over the reported typical values. For example, the typical classes of chromophores where donors and/or acceptors are being varied have slopes of approximately 6 [64,65], and the slopes of the (dicyanomethylene)pyran derivatives with C_{2v} symmetry are close to 10 [29]. Therefore, these results suggest that hydrogen-bond-directed-linking approach provides a new strategy to balance the tradeoff of nonlinearity-transparency.

Although we concerned one-dimensional structures, real materials are three-dimensional. For the material design studies, it is important to consider the impact of packing molecules in the directions perpendicular to the chain backbone. We found that hydrogen bond interaction is stronger than other intermolecular interaction in molecule aggregates, which indicates that the aggregates are preferred to parallel packing. Furthermore, we designed the model systems to investigate the effect of packing on nonlinearity-transparency. From Fig. S1 and Table S6 in Supplementary material,

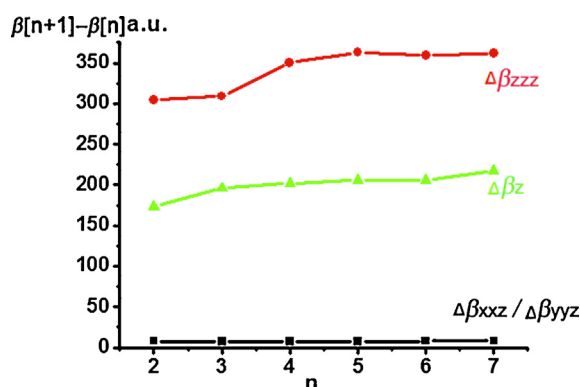


Fig. 4. The change of the first hyperpolarizabilities $\beta_{n+1}-\beta_n$.

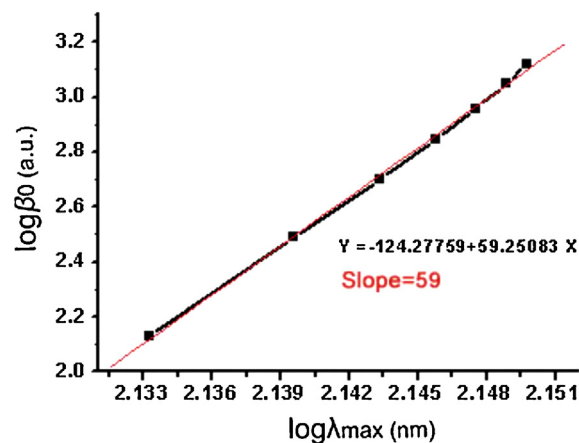
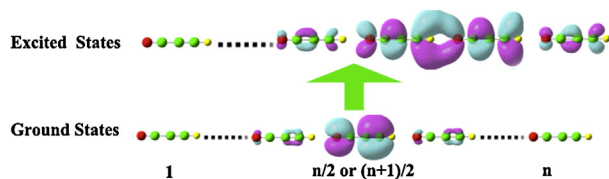


Fig. 5. Nonlinearity-transparency plot.

Table 3The solvent effect on first hyperpolarizability for $(\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H})_n$.

Solvent		Polarity	β_0 (a.u.)
1	C_6H_{12} (cyclohexane)	0.1	885
2	C_6H_6 (benzene)	3	912
3	THF (tetrahydrofuran)	4.2	1096
4	Acetone	5.4	1162
5	DMSO (dimethyl sulfoxide)	7.2	1186

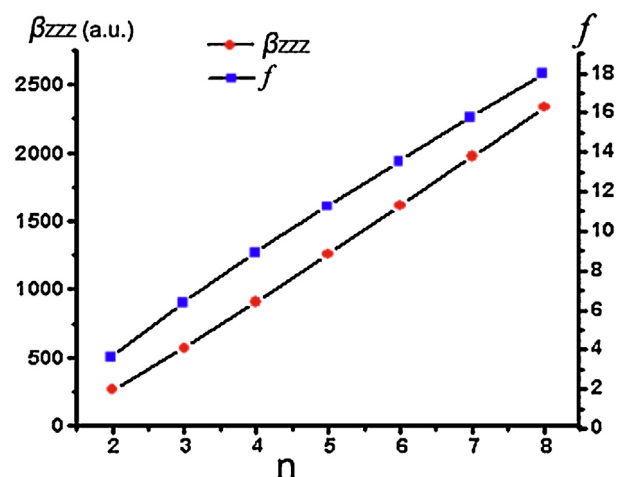
**Fig. 6.** The sketchy crucial transitions.

we found that the parallel packing would not strongly affect the static first hyperpolarizabilities of molecule aggregates and their transparency, because the charge transitions deciding the electronic properties occur along the chain backbone.

In addition, we have employed a polarized continuum method (PCM) to discuss the solvent effect on the structure and first hyperpolarizability. The solvents of cyclohexane (1), benzene (2), tetrahydrofuran (3), acetone (4) and dimethyl sulfoxide (5) are considered. Taking $(\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H})_5$ as a example, we found that the hydrogen bond structure can persevere the linear structure regardless of the solvents, moreover, the solvent with large polarity leads to larger first hyperpolarizability (see Table 3).

3.3. Double degenerated charge transition and strongly coupled oscillators

From Table 2, the unusually large nonlinearities and oscillator strengths suggest that one-dimensional structures have double degenerated charge transitions with strongly coupled oscillators, each providing a contribution to β with the same sign. Accordingly, we calculated the crucial transitions between the ground state and the excited state, as depicted in Fig. S2 in Supplementary material. Their sketchy presentation is shown in Fig. 6. Obviously, similar crucial transitions are found from the middle part to the right end of the one-dimensional structures. By examining the molecular orbitals of the ground state and the given excited state, one can easily determine that there exist double degenerated charge transitions. For our investigated one-dimensional structures with $C_{\infty v}$ symmetry, they have two orthogonal π_{2px} and π_{2py} orbitals from $2p_x$ and $2p_y$ atomic orbitals of N or C atom, respectively. What is more important to us, is that the transitions from each π_{2px} and π_{2py} orbitals of the ground states to the excited states follow the same trend along z axis (C_{∞} axis), therefore, double degenerated charge transitions contribute to the molecular hyperpolarizability β in an additive manner. On the other hand, as shown in Fig. 7, the oscillator strengths f and the β , especially for the tensor β_{zzz} , both increase in the same rhythm, which indicate that the oscillator strength is one decision factor for the molecular hyperpolarizability. Two-level model involving other two factors are the transition energy and the dipole moment difference between the ground states and the excited states $\Delta\mu$. However, from Table 2, we can find that the change of the transition energy is imperceptible. And by analyzing the crucial transition in Figs. 6 and S1 in Supplementary material, one can conclude that the transitions associating with a short distance possess a small $\Delta\mu$ value. Therefore, the huge oscillator strengths are fascinating and striking. As shown in Table 2, estimations of their oscillator strengths are all far above

**Fig. 7.** The tensor β_{zzz} depends on oscillator strengths f .

1.0, which indicates that the one-dimensional cyanoacetylene $(\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H})_n$ by hydrogen-bond-directed-linking have strongly coupled oscillators. Those coupled oscillators come from degenerated π_{2px} and π_{2py} orbitals. Moreover, the coupled oscillator strengths become stronger with the incensement of n , due to more π electrons participating in the couple situation.

4. Conclusions

In summary, the one-dimensional polymeric cyanoacetylenes $(\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H})_n$ ($n = 2-8$) by hydrogen-bond-directed-linking were investigated. Theory calculation shows that they exhibited enhanced first hyperpolarizability and very little red-shifts with the increase of n . Thus, hydrogen-bond-directed-linking approach was expected as a new strategy to balance the tradeoff of nonlinearity-transparency. We proposed that the one-dimensional structures possess double-degenerated charge transitions, both contributing to the hyperpolarizability in an additive fashion, and that they have gradually enhanced coupled oscillators, which leads to the enhanced increase of the first hyperpolarizability. Therefore, in this paper, we hope that hydrogen-bond-directed-linking is helpful to design NLO materials with excellent transparency-efficiency.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jmngm.2014.07.015>.

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