



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



Fang Ma<sup>a,\*</sup>, Dong-Sheng Bai<sup>a,1</sup>, Hong-Liang Xu<sup>b,\*\*</sup>

<sup>a</sup> School of Chemistry and Materials Science, Huaibei Normal University, Huaibei 235000, China

<sup>b</sup> Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, China

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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  $\pi$ -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  $\beta$  by optimizing donor/acceptor moiety strengths and/or extending  $\pi$ -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  $\beta_0$  is proportional to oscillator

strength for the single transition multiplied by the third power of the absorption maximum  $\lambda_{\text{max}}^3$ , and in generally, the  $\lambda_{\text{max}}$  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  $\beta$  [24]. Moreover, most one-dimensional D– $\pi$ –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  $\Lambda$ -shape molecules, owing to the large off-diagonal  $\beta$ -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– $\pi$ –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

\* Corresponding author. Tel.: +86 05613802335.

\*\* Corresponding author. Tel.: +86 043185684009.

E-mail addresses: [mafangchem@foxmail.com](mailto:mafangchem@foxmail.com) (F. Ma), [hlixu@nenu.edu.cn](mailto:hlixu@nenu.edu.cn) (H.-L. Xu).

<sup>1</sup> Tel.: +86 05613802335.

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  $XH \cdots Y$ , 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  $C-H \cdots Y$  hydrogen bonds involving electronegative atoms, anions, or  $\pi$ -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  $4.238 \times 10^{-30}$  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  $\beta_{tot}$  is  $3.11 \times 10^{-29}$  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  $\pi$ -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  $C_3HN \equiv C \equiv C-H$ , 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 ( $N \equiv C-C \equiv C-H$ ) $_n$  by hydrogen-bond-directed-linking.

In this paper, we described our studies on one-dimensional polymeric cyanoacetylene ( $N \equiv C-C \equiv C-H$ ) $_n$  ( $n=2-8$ ) 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, ( $N \equiv C-C \equiv C-H$ ) $_n$  can exhibit first hyperpolarizability and little red-shift, which is helpful to solve the transparency-efficiency tradeoff. We presented the evidences that the excellent  $\beta_0$  values are due to the existence of double-degenerated charge transition states, which contribute to  $\beta_0$  in an additive manner. Thus, by using hydrogen-bond-directed-linking method, we can obtain one-dimensional structure ( $N \equiv C-C \equiv C-H$ ) $_n$ , exhibiting gradually enhanced first hyperpolarizability with little red-shift.

## 2. Computational methods

First, considering the dimer ( $N \equiv C-C \equiv C-H$ ) $_2$  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 ( $N \equiv C-C \equiv C-H$ ) $_n$  ( $n=2-8$ )

can be polymerized by hydrogen-bond-directed-linking. The optimized geometric structures of ( $N \equiv C-C \equiv C-H$ ) $_n$  ( $n=2-8$ ) 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 ( $N \equiv C-C \equiv C-H$ ) $_1$  and ( $N \equiv C-C \equiv C-H$ ) $_{n-1}$  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):

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

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

The (hyper)polarizabilities of ( $N \equiv C-C \equiv C-H$ ) $_n$  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  $N \equiv C-C \equiv C-H$  (see Table S1 in Supplementary material). Second, taking a medium structure ( $N \equiv C-C \equiv C-H$ ) $_5$  as an example, a detail discussion about the difference of  $\beta$  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 ( $N \equiv C-C \equiv C-H$ ) $_n$ , including the transition energy  $\Delta E$  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,  $\mu$  is the component of the dipole moment vector,  $\alpha$  is the linear polarizability tensor,  $\beta$  and  $\gamma$  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 ( $\mu_0$ ) and polarizability ( $\alpha_0$ ) 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

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

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

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