Supporting Information

### Exploring the Novel Donor-Nanotube Archetype as Efficient Third- Order Nonlinear Optical Material: Asymmetric Open-Shell Carbon Nanotubes

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**Figure S1**. Geometrical parameters for optimized (6,0)<sub>3</sub> BNNT and CNT at spin unrestricted (U) B3LYP/6-31G\* level of theory

#### **Comparison of Molecular Geometries of BNNTs and CNTs**

The optimized molecular geometries for  $(6,0)_3$  BNNT and CNT are illustrated in Figure S1 together with a comparison of radial and vertical bond lengths. It can be seen that the diameter of  $(6,0)_3$  CNT is 4.851 Å, while  $(6,0)_3$  BNNT possesses two dimeters, i.e., N-edge (5.096Å) and B-edge (4.831Å). The four radial B-N bonds are 1.456Å, 1.458Å, 1.459Å and 1.454Å for R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>, respectively, in  $(6,0)_3$ BNNT. Similarly, the three vertical B-N bonds of BNNT are also shown to possess different lengths as 1.452Å, 1.449Å and 1.451Å for T1, T2 and T3, respectively. In contrast, such bond length alternations are not prominent for C-C bonds in  $(6,0)_3$  CNT as seen in Figure S1. Another important difference is found in electronic dipole moments for  $(6,0)_3$  CNT and  $(6,0)_3$  BNNT. The dipole moment of  $(6,0)_3$  CNT is found to be zero due to its symmetric change distribution, while for dipole moment of 8 Debye is found for  $(6,0)_3$  BNNT that is probably due to its local dipoles for individual B-N bonds owing to the electronegativity difference of Nitrogen and Boron atoms.



**Figure S2**. Mulliken atomic charges of individual atoms in color scheme along with their dipole moments at spin unrestricted (U) B3LYP/6-31G\* level of theory



**Figure S3**. Odd electron densities corresponding to diradical characters  $y_i$  for CNT(6,0)<sub>1</sub> calculated at LC-UBLYP/6-31G\* level of theory. The yellow iso-surfaces represent densities with iso-surface of 0.001 a.u. (i = 0) and 0.0005 a.u. (i = 1, 2).

## Derivation of the seven-point formula for the fourth-order numerical difference in the finite-field method

#### Definitions of (hyper)polarizability tensors

The electronic polarization p under the static electric field F can be represented as the following power series expression:

$$p = \mu - \mu_0 = \alpha F + \beta F F + \gamma F F F + \cdots.$$
(S1)

Here,  $\alpha$ ,  $\beta$ , and  $\gamma$  are the polarizability, first hyperpolarizability and second hyperpolarizability, respectively.  $\mu$  and  $\mu_0$  are the dipole moment vectors with and without the electric field, respectively. For the *i*-axis component, we have

$$p^{i} = \mu^{i} - \mu_{0}^{i} = \sum_{j} \alpha_{ij} F^{j} + \sum_{jk} \beta_{ijk} F^{j} F^{k} + \sum_{jkl} \gamma_{ijkl} F^{j} F^{k} F^{l} + \cdots$$
, (S2)

where the superscript *i* represents the *i*-axis component of the vector. Eq. (S2) can be rewritten as,

$$\mu^{i} = \mu_{0}^{i} + \sum_{j} \alpha_{ij} F^{j} + \sum_{jk} \beta_{ijk} F^{j} F^{k} + \sum_{jkl} \gamma_{ijkl} F^{j} F^{k} F^{l} + \cdots$$
(S3)

In the presence of external static field, the total electronic Hamiltonian  $\hat{H}(F)$  within the electric dipole approximation is,

$$\hat{H}(F) = \hat{H}_0 - \hat{\mu} \cdot F, \tag{S4}$$

where  $\hat{H}_0$  and  $\hat{\mu}$  are the field-free Hamiltonian and the electronic dipole operator, respectively. By applying the Hellmann-Feynman theorem, the differentiation of the expectation value of the Hamiltonian (S4) gives the following relation:

$$\frac{\partial E(F)}{\partial F^{i}} = \left\langle \Psi(F) \left| \frac{\partial \hat{H}(F)}{\partial F^{i}} \right| \Psi(F) \right\rangle = \left\langle \Psi(F) \left| -\hat{\mu}^{i} \right| \Psi(F) \right\rangle = -\mu^{i}.$$
(S5)

Here we assumed the following Schrödinger equation,

$$\hat{H}(F)|\Psi(F)\rangle = E(F)|\Psi(F)\rangle.$$
(S6)

From eqs. (S3) and (S5), we have,

$$E(F) = E(0) - \sum_{i} \mu_{0}^{i} F^{i} - \frac{1}{2} \sum_{j} \alpha_{ij} F^{i} F^{j} - \frac{1}{3} \sum_{jk} \beta_{ijk} F^{i} F^{j} F^{k} - \frac{1}{4} \sum_{jkl} \gamma_{ijkl} F^{i} F^{j} F^{k} F^{l} + \cdots$$
(S7)

The definition of (hyper)polarizabilities based on the power series of dipole moment is called *B*-convention. Note that if we employ the Taylor series expansion for the dipole moment,

$$\mu^{i} = \mu_{0}^{i} + \sum_{j} \alpha'_{ij} F^{j} + \frac{1}{2!} \sum_{jk} \beta'_{ijk} F^{j} F^{k} + \frac{1}{3!} \sum_{jkl} \gamma'_{ijkl} F^{j} F^{k} F^{l} + \cdots,$$
(S8)

we will obtain a different definition of the (hyper)polarizabilities. This is called *T*-convention, which is usually employed in several quantum chemical program packages such as Gaussian. Difference between the definitions is the prefactor of

each term, e.g.,  $\gamma_{ijkl} = \frac{\gamma_{ijkl}}{3!}$ .

In the present study, we employed the definition of second hyperpolarizability in *B*-convention. If we consider the Taylor series expansion of E(F) around F = 0, then,

$$E(F) = E(0) + \sum_{i} \frac{\partial E(F)}{\partial F^{i}} \bigg|_{F=0} F^{i} + \frac{1}{2!} \sum_{j} \frac{\partial^{2} E(F)}{\partial F^{i} \partial F^{j}} \bigg|_{F=0} F^{i} F^{j}$$

$$+ \frac{1}{3!} \sum_{jk} \frac{\partial^{3} E(F)}{\partial F^{i} \partial F^{j} \partial F^{k}} \bigg|_{F=0} F^{i} F^{j} F^{k}$$
  
+ 
$$\frac{1}{4!} \sum_{jkl} \frac{\partial^{4} E(F)}{\partial F^{i} \partial F^{j} \partial F^{k} \partial F^{l}} \bigg|_{F=0} F^{i} F^{j} F^{k} F^{l} + \cdots$$
 (S9)

So, by comparing each term of eqs. (S7) and (S9), we have the following relations,

$$\alpha_{ij} = -\frac{\partial^2 E(F)}{\partial F^i \partial F^j} \bigg|_{F=0},$$
(S10)

$$\beta_{ijk} = -\frac{1}{2!\partial F^i \partial F^j \partial F^k} \bigg|_{F=0},$$
(S11)

$$\gamma_{ijkl} = -\frac{1}{3! \partial F^{i} \partial F^{j} \partial F^{k} \partial F^{l}} \bigg|_{F=0}$$
(S12)

which can be used for the numerical difference of the total energy. Now we consider the diagonal component of second hyperpolarizability,

$$\gamma_{iiii} = -\frac{1}{3!} \frac{\partial^4 E(F)}{(\partial F^i)^4} \Big|_{F=0}$$
(S13)

which is calculated form the fourth order derivative of the total energy with respect to the field.

# Derivation of the seven-point numerical difference formula for the fourth-order derivative

For simplicity, we consider a function f(x) which can be expressed as the Taylor series around  $x_0$ , i.e.,

$$f(x) = f^{(0)}(x_0) + f^{(1)}(x_0)(x - x_0) + \frac{1}{2!}f^{(2)}(x_0)(x - x_0)^2 + \frac{1}{3!}f^{(3)}(x)(x - x_0)^3 + \frac{1}{4!}f^{(4)}(x)(x - x_0)^4 + \cdots$$
(S14)

Here  $f^{(n)}(x)$  is the *n*th-order derivative of f(x). Assume that *h* is a small change of the variable *x* and *n* is the natural number. By substituting  $x = x_0 \pm nh$ , eq. (S14) becomes

$$f(x_0 \pm nh) = f(x_0) \pm nf^{(1)}(x_0)h + \frac{n^2}{2!}f^{(2)}(x_0)h^2 \pm \frac{n^3}{3!}f^{(3)}(x_0)h^3 + \frac{n^4}{4!}f^{(3)}(x_0)h^4 \pm \cdots$$
(S15)

So, we have the following equations,

$$f(x_0 + nh) + f(x_0 - nh) = 2\left\{f(x_0) + \frac{n^2}{2!}f^{(2)}(x_0)h^2 + \frac{n^4}{4!}f^{(4)}(x_0)h^4 + \frac{n^6}{6!}f^{(6)}(x_0)h^6 + \cdots\right\},$$
 (S16-*n*)

and,

$$f(x_0 + nh) - f(x_0 - nh) = 2\left\{nf^{(1)}(x_0)h + \frac{n^3}{3!}f^{(3)}(x_0)h^3 + \frac{n^5}{5!}f^{(5)}(x_0)h^5 + \cdots\right\}.$$
(S17-n)

From eq. (S17-1), the central difference (two-point formula) for the first-order derivative is obtained as

$$f^{(1)}(x_0) = \frac{f(x_0 + h) - f(x_0 - h)}{2h} + O(h^2).$$
(S18)

By considering a sum of the equations, (S17-2)  $+2^3 \times$  (S17-1), we can to eliminate the main term of  $O(h^2)$  to obtain the following equation,

$$f(x_{0} + 2h) - f(x_{0} - 2h) - 2^{3} \{ f(x_{0} + h) - f(x_{0} - h) \}$$
  
=  $2 \{ 2f^{(1)}(x_{0})h + \frac{2^{3}}{3!}f^{(3)}(x_{0})h^{3} + \frac{2^{5}}{5!}f^{(5)}(x_{0})h^{5} + \cdots \}$   
-  $2 \cdot 2^{3} \{ f^{(1)}(x_{0})h + \frac{1}{3!}f^{(3)}(x_{0})h^{3} + \frac{1}{5!}f^{(5)}(x_{0})h^{5} + \cdots \}$   
=  $-2 \{ 6f^{(1)}(x_{0})h + \frac{24}{5!}f^{(5)}(x_{0})h^{5} + \cdots \}$ . (S19)

Thus, we obtain the following four-point formula

$$f^{(1)}(x_0) = \frac{-\{f(x_0+2h) - f(x_0-2h)\} + 8\{f(x_0+h) - f(x_0-h)\}}{12h} + O(h^4)$$
(S20)

We can apply similar procedures for the derivation of the higher-order derivatives, although we also need to eliminate the lower-order derivative terms. For the fourth-order derivative, we firstly consider a sum of the equations, (S16-2)  $+ a \times$  (S16-1). To eliminate the second-order term including  $f^{(2)}$ , we need to set a condition  $2^2 + a = 0$ , i.e., a = -4. Therefore, the equation becomes

$$f^{(4)}(x_0) = \frac{-\{f(x_0 + 2h) + f(x_0 - 2h)\} + 4\{f(x_0 + h) + f(x_0 - h)\} - 6f(x_0)}{h^4} + O(h^2),$$
(S21)

which gives the five-point formula for the fourth-order derivative. To eliminate the main term of  $O(h^2)$ , we need to consider the equations (S16-*n*) up to n = 3. So, let us consider a sum of the equations, (S16-3)  $+ a \times$  (S16-2)  $+ b \times$  (S16-1). To eliminate the second-order term, we need to set a condition,  $3^2 + 2^2a + b = 0$ . To eliminate the

 $O(h^2)$  term, which corresponds to the sixth-order term, we need to set another condition,  $3^6 + 2^6a + b = 0$ . To satisfy these conditions, the factors must be (a,b) = (-12,39), and then we have

$$f^{(4)}(x_0) = \frac{-\{f(x_0 + 3h) + f(x_0 - 3h)\} + 12\{f(x_0 + 2h) + f(x_0 - 2h)\} - 39\{f(x_0 + h) + f(x_0 - h)\} + 6h^4}{6h^4} + O(h^4)$$
(S22)

as the seven-point formula for the fourth-order derivative.

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#### *Finite-field method for the longitudinal second hyperpolarizability tensor* Considering the numerical accuracy, we apply the seven-point formula, eq. (S22), to evaluate the fourth-order derivative of the total energy in Eq. (S13). Then, we have

$$\gamma_{iiiii} = -\frac{1 - \{E(3F^i) + E(-3F^i)\} + 12\{E(2F^i) + E(-2F^i)\} - 39\{E(F^i) + E(-F^i)\} + 56E(0)}{6(F^i)^4}$$
(S23)

as the working equation of the finite-field method for the calculation of longitudinal second hyperpolarizability tensor. The right-hand-side of the equation is the same as that of eq. (2) in the main text. Note that this formula involves an error of  $O((F^i)^4)$ , and thus the obtained value depends on the amplitude  $F^i$  to be employed. In principle, we can decrease the error by setting a very small finite amplitude. In practical, however, the present situation is not so simple. The numerator consists of the sums and differences of the total electronic energies under several electric fields. The total energy is also calculated numerically within a finite digit number using the quantum chemical program package. To reduce the errors originating in the cancellation of significant digits, we also need to set very tight convergence criterion for the total energy (and the density matrix as well). Since extremely tight convergence criteria may be difficult to achieve, we need to find balanced conditions for the convergence criterion and the field amplitudes. In the present study, we set the convergence criterion for the total energy as 10<sup>-10</sup> a.u., and then evaluate the right-hand-side of eq. (S23) using several different  $F^i$  values to check the numerical accuracy.