## **Electronic Supplementary Information**

#### Connecting Effect on the First Hyperpolarizibility of Armchair Carbon-Boron-Nitride

#### Heteronanotubes: Pattern versus Proportion

Rong-Lin Zhong,<sup>a, b</sup> Hong-Liang Xu\* <sup>b</sup> and Zhong-Min Su\* <sup>b</sup>

<sup>a</sup> Institute of Theoretical Chemistry, Jilin University, Changchun, 130023 Jilin, People's Republic

of China

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

Changchun, 130024 Jilin, People's Republic of China

E-mail: <u>hlxu@nenu.edu.cn</u>, <u>zmsu@nenu.edu.cn</u>

#### 1. Test for Basis Sets

For the effect of basis sets, we have tested four different the basis sets to calculate the static first hyperpolarizability of PA-6. The 6-31g\*, 6-311g\*\*, 6-311+g\*\* and 6-31g for the hydrogen/carbon atoms and the 6-311+g(3df) basis set for the boron/nitrogen atoms were employed. As listed in Table S1, the basis effects on the static first hyperpolarizability are small. Therefore, the first hyperpolarizability is evaluated at CAM-B3LYP/6-31G\* level with considering to the computational cost and accuracy.

**Table S1.** The first hyperpolarizabilities ( $\beta_0$ ) of PA-6 calculated by different basis sets

	6-31g*	6-311g**	6-311+g**	6-31g/6-311+g(3df)
$\beta_{\rm x}$	-1.13×10 <sup>3</sup>	-1.11×10 <sup>3</sup>	-6.04×10 <sup>2</sup>	-1.24×10 <sup>3</sup>
$eta_{ ext{y}}$	1.40×10 <sup>3</sup>	1.35×10 <sup>3</sup>	2.04×10 <sup>3</sup>	1.40×10 <sup>3</sup>
$\beta_{\rm z}$	-1.99×10 <sup>4</sup>	-2.18×10 <sup>4</sup>	-2.31×10 <sup>4</sup>	-1.87×10 <sup>4</sup>
$\beta_0$	2.00×10 <sup>4</sup>	2.18×10 <sup>4</sup>	2.32×10 <sup>4</sup>	1.89×10 <sup>4</sup>

## 2. Effect on polarizability

**Figure S1.** The relationship between the static first polarizability ( $\alpha_0$  au) and carbon proportion of armchair BNCNT with different connecting patterns



### 3. The structures of CA-n, HA-n and PA-n models

Figure S2. The CA-n, HA-n and PA-n models with different carbon proportion (n=2, 4, 6 and 8)



Hydrogen is used as passivated atom on the periphery, which is not shown

#### 4. The charge density distribution

Figure S3. The charge density distribution plot of PA-6, HA-6 and CA-6



In the charge density distribution plot, the dark blue and light blue parts correspond to the region where electron density is increased and decreased after electron excitation, respectively. As shown in Figure S3, a conspicuously charge transfer character is exhibited (from the left part (B-connecting carbon atoms) to right part (N-connecting carbon atoms) of the figure) in PA-6. Correspondingly, a helical charge transfer is also found in HA-6. However, no evident spatial separation between hole and electron was shown in CA-6, exhibiting that the transition mode is a local excitation character, which is different from the other two isomers.

# 5. The DOS of the pristine CNT and BNNT

Figure S4. The DOS of pristine CNT and BNNT cluster models



#### 6. Comparison with the cluster model and the periodic boundary conditions model

In this work, the main calculations were based on cluster models in which the atoms on the periphery were saturated by hydrogen atoms. To study the effects of the nanotube termination, we performed a test calculation by considering the one-dimensional periodic boundary conditions (PBC) along the tube axis to simulate infinitely long ternary carbon-boron-nitride heteronanotubes with the Vienna Ab initio Simulation Package<sup>1</sup> (VASP). The Perdew-Burke-Enzerhof<sup>2</sup> (PBE) exchange-correlation functional, all-electron plane-wave basis sets with an energy cutoff of 400 eV, and the projector augmented wave (PAW<sup>3</sup>) method have been adopted. The Brillouin-zone of the supercell was sampled by  $1 \times 1 \times 3$  k-points using the Monkhorst–Pack<sup>4</sup> scheme, and first-order Methfessel-Paxton smearing of 0.2 eV was employed in the integration to speed up the convergence. We calculated the band gap of PA models with different carbon proportion according to the one-dimensional periodic boundary conditions. The relationship between the band gap and carbon proportion is shown in as the following figure (red line). On the other hand, the HOMO-LUMO gap of the cluster models is also shown (black line). The test calculation exhibits consistency on the energy gap between the PBC and cluster models. On the other hand, the energy gap increases 0.29-0.65 eV by the saturated hydrogen atoms as shown in Figure S5 (ESI)

**Figure S5.** The HOMO-LUMO gap based on the cluster models and the band gap based on PBC models



# References

- 1. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, 54, 11169-11186.
- 2. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-

3868.

- 3. P. E. Blöchl, Phys. Rev. B, 1994, 50, 17953-17979.
- 4. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, 13, 5188-5192.