Second-Harmonic Generation of Organic Molecules Encapsulation within Boron Nitride Zigzag Nanotubes

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Abstract

We present ab initio calculations to investigate the absorption properties and the second harmonic generation (SHG) response, of three amino acids and four nitrogeneus bases: glycine, serine, cysteine, guanine, uracil, thymine and cytosine on the inner surface of boron nitride nanotubes (BNNTs). The nanotube that encapsulate the molecules is zigzag (12,0) BNNT B72N72H24 . At first, we study the behavior of the binding energy of this organic molecules with the inner walls of the BNNT, we also calculate the electronic Density of States (DOS) for each optimized structure. Calculations have been performed using density functional theory (DFT) using Generalized Gradient Approximation (GGA). Evaluation of the static linear polarizability and SHG response for the wavefunctions, was performed by applying finite electric fields.

Method

Each molecule was placed inside a BNNT to obtain the optimized structure using General Atomic and Molecular Electronic Structure System (GAMESS) [1]. On every case, hydrogen atoms were added to saturate free bonds on both sides of the BNNT, so the optimization can be performed.
For the calculation we used Density Functional Theory (DFT) using Generalized Gradient Approximation (GGA). Also, we used Restricted Hartree-Fock method (RHF) and a Gaussian basis 6-31G. Moreover, we used the functional B3LYP, which is a hybrid of exact Hartree-Fock exchange with local gradient-corrected exchange and correlation terms, as first suggested by Becke (1993).
Convergence of Self Consistent Field (SCF) is achieved when the density change between two consecutive SCF cycles is less than $3.0x10^{-5}$ in absolute value.
Convergence of a geometry search is reached when the largest component of the gradient is less than $3.0x10^{-4}$ (Hartree/Bohr) and the Root Mean Square (RMS) gradient less than $1.0x10^{-4}$.
The binding energy (E_b) of the optimized structure is calculated by

$$E_b = E_{BNNT+m} - E_m - E_{BNNT} \qquad (1)$$

Then, the electronic DOS was calculated for each optimized structure; followed by the calculation of the SHG response, which was performed applying finite electric fields, also with the GAMESS code.

Results

The binding energies for each structure are shown in table 1.

BNNT encapsulating:	Binding energy (eV) our results	Binding energy (eV) Results from [2]
Glycine	0.280	-0.098
Serine	0.311	-0.21
Cysteine	0.275	-0.078
Cytosine	0.397	0.031
Thymine	0.265	0.55
Uracil	0.273	0.0066
Guanine	0.297	0.037

Table 1. Binding energies for organic molecules encapsulated by a zigzag (12,0) BNNT.

We note that there is no absorption or bonding between the molecules and the BNNT, acording to Equation (1). Optimized structures for BNNT encapsulating glycine, guanine, cytosine and uracil are shown on fig. 1 end their corresponding DOS are shown in fig. 2

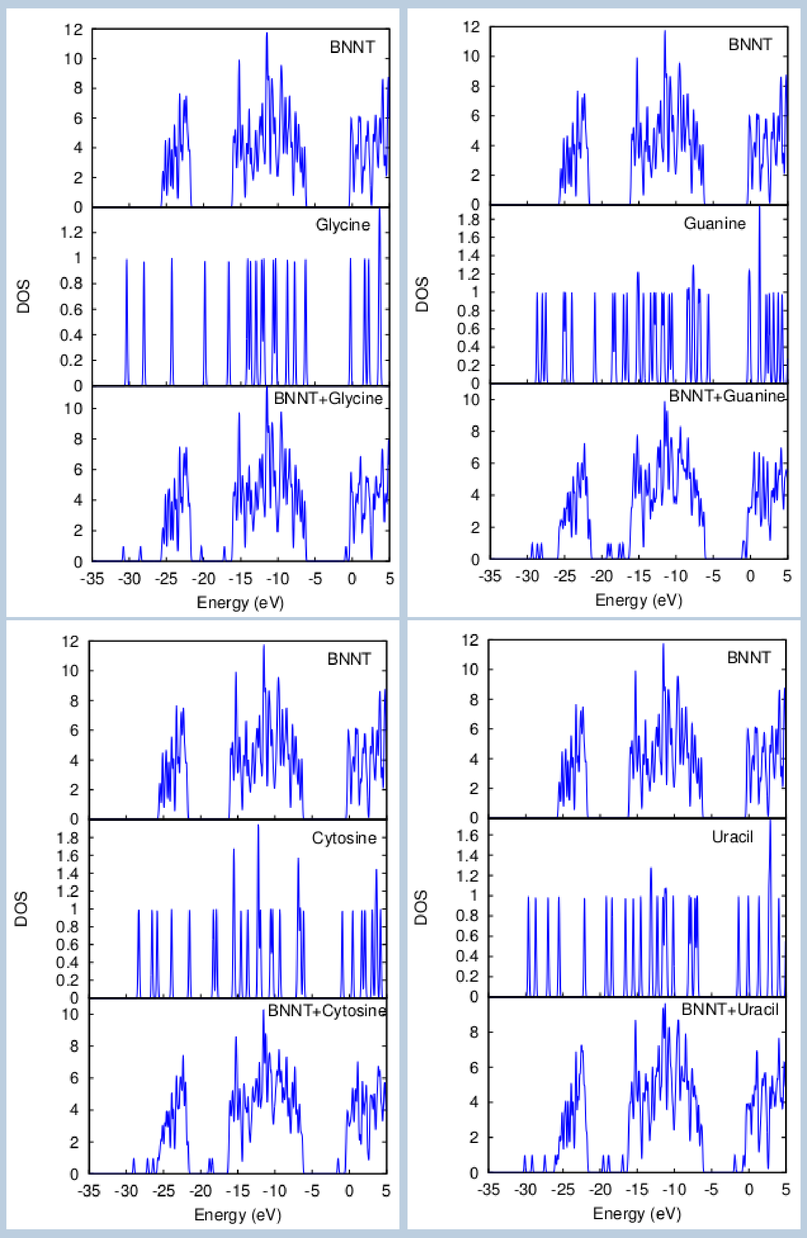

Figure 2. DOS calculated for BNNT encapsulating glycine, guanine, cytosine and uracil. Top panel: pristine zigzag (12,0) BNNT, middle panel: isolated molecule, and bottom panel: BNNT encapsulating the molecule.

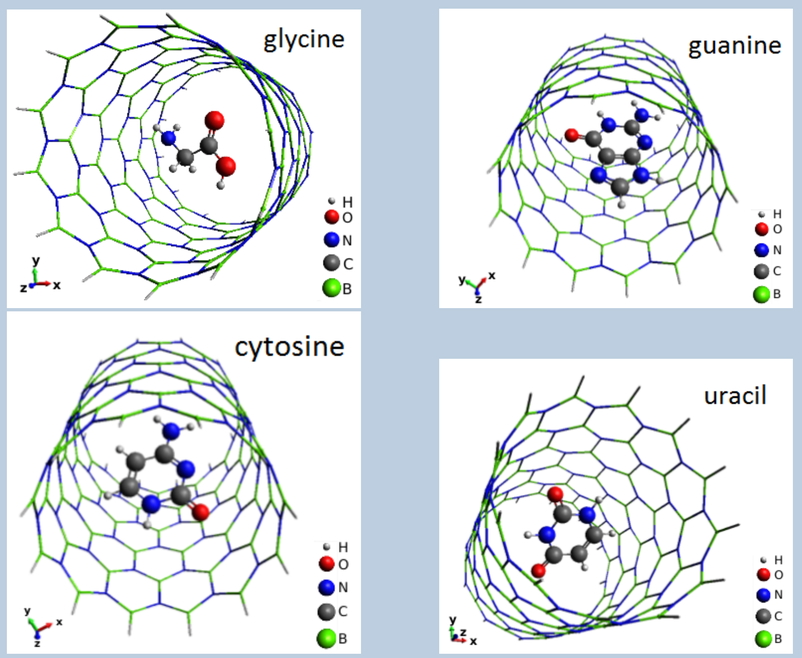

Figure 1. Zigzag (12,0) BNNT encapsulating glycine (top left), guanine (top right), cytosine (bottom left) and uracil (bottom right).

We observed that the DOS showed on figure 2 seems to be the sum of the top and middle panels with a slight shift of energy levels of the molecule. This means that the change of the electronic structure of the BNNT and the molecule after the encapsulation is negilible.
We calculated the SHG susceptibility $\chi^2(-2\omega;\omega,\omega)$ of the BNNTs with $\omega = 455nm$. The point symmetry group of zigzag (n,0) NT is C^{22}_{2nv}.
A very intense linear optical response is only observed for light polarized along the tube axis (z), since in the case of perpendicular polarization, the linear absorption is suppressed by strong depolarization effects[4]. Following this observation, we only consider the $\chi^{zzz}(-2\omega;\omega,\omega)$.

BNNT encapsulating:	$\chi^{zzz}(0;0,0)$	$\chi^{zzz}(-2\omega;\omega,\omega)$
Glycine	-507.49	-918.82
Serine	-490.19	-894.22
Cysteine	-491.12	-845.73
Cytosine	-462.52	-786.53
Thymine	-450.61	-781.21
Uracil	-482.54	-833.69
Guanine	-456.09	-598.75

Table 2. Average static polarizability and SHG response on the z axis corresponding to $\omega = 455nm$ (a.u.).

In Table 2, we report the calculated average static polarizability and first hyperpolarizability for all cases. Changing the radius of the BNNTs, we note that the static value of $\chi^{zzz}(0;0,0)$ increases as the radius of the NT decreases, same as $\chi^{zzz}(-2\omega;\omega,\omega)$.

Conclusions

According to our calculations, there is no absortion between organic molecules and BNNTs; as a result, BNNTs can be used in medical applications like drug dispensation with high presition beacuse of the chemically inert nature of BNNTs.
We found that the static value, $\chi^{zzz}(0;0,0)$, increases as the NT radius decreases. The SHG susceptibility ab initio data obtained shows values acording to espectation, and also we found that $\chi^{zzz}(-2\omega;\omega,\omega)$ increases as the NT radius decreases. We expect that our results may motivate the experimentalist community to investigate nonlinear optical properties of these class of NTs.

Acknowledgements

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