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Charges Transfer in Quater-Thiophene Confined in Graphene Using the Infrared Calculations

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ABSTRACT

In this theoretical work, we study the polarIzed infrared spectra of hybrid nanostructures obtained by confinement of quater-thiophene (4T) in multi-layered graphene in the framework of spectral moments method. To derive the optimum configurations of 4T intercalated in graphene, the minimum energy calculations using a convenient Lennard-Jones expression of the van der Waals intermolecular potential is devoted. We found a parallel configuration of quater-thiophene molecule with respect to the graphene plane. A significant charge transfer on the inserted quater-thiophene was found by analyzing the infrared spectroscopy. This charge transfer due by the change of the G-band intensity and the low-frequency modes vanishing.

Keywords: *Graphene, IR Spectroscopy, Thiophene, Charge transfer*

INTRODUCTION

Carbon nanomaterials like carbon nanotubes [1] and graphene [2] have optical and electrical properties that make them ideal nanoscale materials [3-5]. Currently, they are being studied for use in new technologies for energy conversion (e.g., solar cells and fuel cells) and energy storage (e.g., supercapacitors and batteries) [6, 7].

In other hand, the low power conversion efficiency of the organic solar cells presents the main handicap for these devices. The introduction of graphene is the alternative method to solve this handicap to form an interpenetrating blend with the polymer. Since the discovery of photoinduced charge transfer between organic conjugated polymers (as donor) and graphene (as acceptor), graphene has been used to fabricate photovoltaic devices in combination with different polymers to the aim of increasing the power conversion efficiency [8, 9]. The process consists of intercalating oligomers between two sheets of graphene in order to keep their original physical properties [10, 11]. The advantage of this method is that the graphene protects the internal organic molecules from photo degradation and attacks by external reactive species, thereby preventing undesirable alteration of the organic molecules [12].

Thiophene and its polymerized derivatives are considered as the reference compounds of conjugated polymers widely used in organic electronic devices and recently in novel hybrid graphene materials for solar cell. The non-covalent functionalization of graphene with conjugated polymers molecules provides an elegant approach to elaborate hybrid systems with original physical properties. Several experimental works dealt with the encapsulation of oligothiophene derivatives (oTh) into NTs(oTh@NT) [11, 13]. Indeed, these systems are particularly interesting as the π-conjugation of the thiophene molecules provides nonlinear optical properties and intrinsic electrical conductivity [14-18].

In a previous work [19], the charge transfer in bithiophene (2T) intercalated inside graphene has been investigated. In this work, in order to complete our study in the nT@G hybrid systems, we study the vibrational properties on quater-thiophenes in multi-layered graphene (4T@G) using infrared spectroscopy. The calculations have been performed using the spectral moment's method (SMM) [20, 21].

MODELS AND COMPUTATIONAL METHOD

The minimization energy calculations on quarter-thiophene intercalated between two sheets of graphene performed as follow. We inserted the quarter-thiophene molecule between two graphene layers, where the bottom layer is fixed. The top layer and the inserted molecule positions can vary during our structural relaxation procedure. We found that a favored parallel configuration of 4T inside the graphene bilayer. The optimal graphene layer-quarter-thiophene molecule gap is calculated around 0.349 ± 0.005 nm.

The dynamical matrix of our hybrid system is built block by block from the dynamical matrices of each subsystems: The graphene and oligothiophene forms the tridiagonal block of the dynamical matrix of the hybrid systems. While the interactions of graphene-oligothiophene and graphene-graphene forms the off-diagonal block.

The dynamical matrix of the oligomers molecules is calculated using DFT as implemented inside the Spanish initiative for Electronic Simulations with Thousands of Atoms (SIESTA) package [22]. Core electrons were replaced by nonlocal norm-conserving pseudo-potentials. The valence electrons were described by a double-ζ singly polarized basis set. The localization of the basis is controlled by an energy shift of 50 meV. Real space integration was performed on a regular grid corresponding to a plane-wave cutoff around 360 Ry. The first Brillouin zone was sampled according to the Monkhorst-Pack scheme by using 10 k-points along the molecule direction. We considered a vaccum size of 12Å to avoid interactions between adjacent systems.

The dynamical matrIx of graphene sheets is computed from the force constant model introduced by Saito et al. [23]. This model was previously used by our group to study the nonresonant Raman spectra of single-walled carbon nanotubes (SWNTs) and double-walled carbon nanotubes (DWNTs) as a function of their lengths [24-28]. The interactions between oligomer-graphene are described according to the van der Waals potential. We choose a Lennard-Jones type :

$$U_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

with parameters: ε= 2.964 meV and σ= 0.3407 nm for carbon atoms. ε= 10.7 meV and σ = 0.3560 nm for sulfur atoms. ε = 0.67 meV and σ = 0.1069 nm for hydrogen atoms.

The Sulfur-Carbon and Carbon-Hydrogen parameters were calculated using the rule of mixtures of Lorentz-Berthelot: $\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}$ and $\sigma_{AB} = (\sigma_A + \sigma_B)/2$.

RESULTS

a. Infrared spectra of graphene and free 4T oligothiophenes as presented in a previous work [19]. The polarized Iz infrared spectrum of graphene is dominated by the tangential mode (TM) located at 1588 cm^{-1}. Concerning the Ix polarization, we found the band around 864cm^{-1}. Many experimental and theoretical infrared studies have shown that the TM frequency follows a dependence as a function of the number of sheet of graphene. This dependence is well reproduced by Saito empirical force field [23].

The infrared spectrum of a free quater-bithiophene (4T) molecule have been intensively studied in the literature [29]. Our frequencies, calculated using DFT are close to those obtained in Ref [29]. From spectra of 4T molecule, in the low region we found a peak around 18 and 22 cm^{-1} corresponding to a libration modes. In the region between 600 and 1600 cm^{-1}, the most intense bands of the oligotiophene are found in this region which are the C-S-C deformation 837 cm^{-1}, the C-H bending 1047 cm^{-1}, the C-C inter-ring stretching 1322 cm^{-1}, and C=C stretching 1503 cm^{-1}.

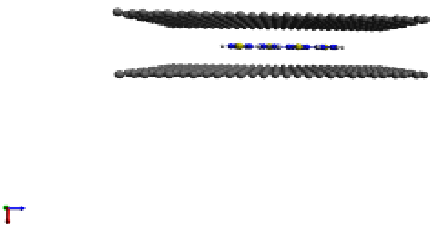

Figure1. *Structure of 4T@G*

b. Infrared spectra of hybrid system (4T@G) The ground state energy of oT@G depends on the oT positions and orientations between the two sheets of graphene. We consider in our calculations that the molecules are parallel to the sheets of graphene figure1. The optimum distance between 4T molecule and graphene sheet is about 0.349nm and distance graphene-graphene about 0.688nm.

We investigate the infrared spectra of the 4T@G hybrid system. The figure2 presents the Iz polarization spectra of 4T molecule (bottom) and 4T@G (top). From the spectra, as we can see the modes located in the lower frequency range are very sensitive to the intercalation of quarter-thiophene into graphene layers. The major changes of frequencies and intensities are observed in this region. First, we observe that the libration mode 18cm^{-1} of 4T molecule disappears in the infrared spectrum of 4T@G system. We observe also a frequency shift of the other modes of 4T@G with respect to the corresponding modes of 4T.

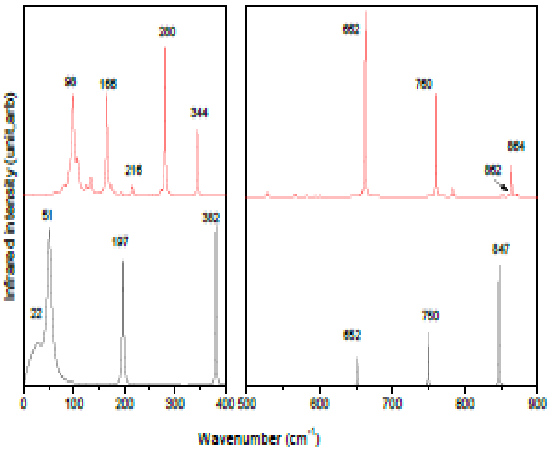

Figure2. *The Ix(ω) infrared spectra of 4T molecule (bottom) and 4T@G hybrid (top).*

In the TLM range, an slightly upshift of the modes in 4T@G with respect to the corresponding modes of 4T molecule is observed. New mode appears at 1589 cm^{-1}. In the Ix polarization the figure3 displays infrared spectra of 4T molecule (bottom) and 4T@G system (top). As observed in the Iz polarization, the mode of libration around 31 cm^{-1} of 4T molecule disappears in the infrared spectrum of 4T@G system. An upshift of the other modes of 4T@G with respect to those of 4T molecule is istablished.

In the intermediate range, the infrared spectrum of 4T@G system shows several lines due to van der Waals inter- actions. An upshift of the all modes by (2 cm^{-1} or 3 cm^{-1}) in 4T@G with respect to those in 4T molecule.

Now, in order to investigate the charge transfer effect in the spectrum of the hybrid system (4T@G). We present in figure4, the Iz polarization infrared spectra of the 4T@G hybrid system using two charge models. In first model we assume transferability of 4T-charges and graphene-charges loads in 4T@G (red line), in the second one we directly calculated the charges configuration of 4T@G (blue line).

The intensities are normalized by the 1328 cm^{-1} mode to compare the two spectra. As we can see the most changes is in the 600-900 cm^{-1} region corresponding to the C-S-C deformation. The IR spectrum of 4T@G sample state that 4T oligomers undergo a significant charge transfer when they are inserted inside graphene layers.

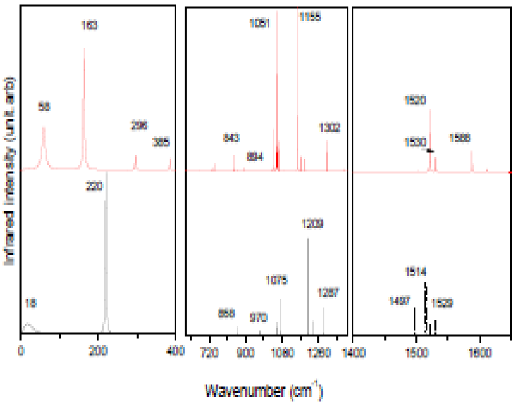

Figure3. *The Iz(ω) infrared spectra of 4T molecule (bottom) and 4T@G hybrid (top).*

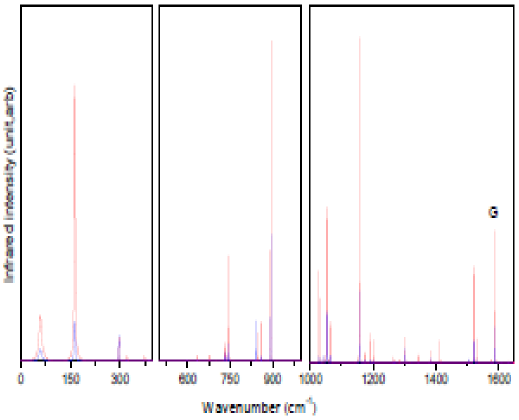

Figure4. *The Iz(ω) infrared spectra of the hybrid system (4T@G) using the charge model of the isolated molecule 4T and graphene (blue) and charge model of 4T in presence of graphene (red). The intensities were normalIzed by the intensity of 1328 cm−1 mode.*

CONCLUSION

In this article, the intercalation of the quarter-thiophene between graphene layers, which gives rise to 4T@G nanohybrids, has been investigated. The optimal configuration of 4T in multi-layered graphene are derived using a convenient Lennar-Jones potential. A hybrid approach is set out to build a dynamic model of 4T@G systems. This approach combines density of functional theory (DFT) and molecular dynamics. After calculations, we found that the 4T molecule adopt a parallel orientation with graphene. Then, for obtained configurations of 4T@G, the infrared spectra have been calculated using the spectral moment's method. We showed that the major changes obtained in the low frequency range. The libration modes in the 4T are disappeared in the Raman spectrum of 4T@G. Also the IR spectra of the 4T@G suggests a significant charge transfer of the oligomers intercalated between graphene layers.

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