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First-principles calculations of the indigo encapsulation and adsorption by MgO nanotubes

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We have performed ab-initio calculations to investigate the structural and electronic properties of (m,m) chiral magnesium oxide nanotubes, (m,m)MgONTs, to explore the encapsulation, inclusion, and adsorption of dyes (organic molecules) such as Indigo (IND). Studies start by determining the structural parameters of the MgO nanotubes with different diameters and the IND. The indigo encapsulation into the MgONT is studied considering four (m,m) chiralities which yield 4 different NT diameters. In the endohedral functionalization, the indigo is within the NT at a tilt angle as in previous theoretical studies of organic molecules inside carbon and boron-nitride nanotubes. Results show that the encapsulation is a strong exothermic process with the m=6 case exhibiting the largest encapsulation energy. It is also explored the indigo adsorption on the NT surface in the parallel and perpendicular configurations. The perpendicular configuration of the IND adsorption on the (8,8)MgONT exhibits the largest energy. The indigo inclusion within the NTs meets a potential barrier when m<6, however this barrier diminishes as the index increases. Additionally, we have determined the total density of states (DOS), partial DOS, electron charge redistributions, and the highest occupied molecular orbital–lowest unoccupied molecular orbital levels for the NTs with m=6. Very strong binding energies and electron charge transfer from the IND to NTs is present in the atomic structures. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4881455]

I. INTRODUCTION

Since the early 90s, with the discovery of carbon nanotubes (CNTs), one-dimensional systems have been the subject of theoretical and experimental investigations provided the systems display unusual properties and potential applications in the electronic and optoelectronic industry.1 In particular, due to the presence of vacuum space along the growth direction and its very large surface area, the single wall carbon nanotubes (SWCNTs) are ideal systems for encapsulating atoms or small molecules. The first evidence of the endohedral functionalization or encapsulation was reported by Takenubo et al.2 In this way, atoms or molecules are isolated of external environment and interact only with the NT walls. The endohedral functionalization by atoms is attractive, however molecules (guest) are currently more interesting, as they may modulate electronic, transport, and optical properties of the host. Not only organic but also organometallic molecules have been studied experimentally and theoretically (including fullerences, fullerene derivatives, alkali metals, and metallocenes3–5) by Lu et al.6 to obtain both p/n-type air stable single wall nanotubes (SWNTs) to control carrier density. Polymerization can also take place inside the CNT.7,8 Boron nitride nanotubes (BNNTs) have been also studied theoretically in the presence of doping with electrophilic and nucleophilic organic molecules (acceptor and donor elements, respectively) which make the BNNT a possible p/n-type semiconductor.9 On the other hand, attention has been paid to the preparation of nanomaterials with the NaCl atomic configuration, such as Magnesium Oxide (MgO). MgO is an inert material with high melting point, due to the large ionic bonding (similar properties to BN), which exhibits a wide band gap of 7.8 eV; MgO has been used as high-temperature superconductor (HTSC) and in thin film coating applications. When systems reduce dimensionality from 3D to 2D materials face new potential technological applications based on the modulation of the band gap as in graphene adsorbed on O/Mg terminated MgO(111) surface.10,11 Moreover, 0D materials such as small-size MgO clusters have been studied experimentally12,13 and theoretically in recent years.14 Finally, magnesium oxide nanotubes (MgONTs), in the rock-salt phase, with chiralities (n,0) and (m,m) have been theoretically investigated15 recently. According to the structural, vibrational, and response properties the MgO (n,0) nanotubes are more stable than those with (m,m) chiralities when n and m are small, however for large diameters both NT families have similar properties as the MgO(001) monolayer. Reference 15 shows that the (m,m) chirality NTs are stable as dictated by the positive vibrational frequencies.

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It is interesting to explore inorganic-organic nanohybrid systems because of technological applications. Examples are the nanopeapod structures which are composed of SWCNTs (pods) and metallic Al₅ clusters, or KI (ionic) crystals to form a composite system. These materials exhibit new physical properties because of the interactions produced by confinement in the one-dimensional cavity. We are interested in this kind of systems as there are nano-composites made-up of clay and dye suitable for the preservation of archaeological buildings, pottery and prehispanic murals in Latin America; particularly it is of interest the ancient nano-hybrid system known as the Maya Blue pigment.

The Maya blue pigment is a composite material, which is a result of the mixing of palygorskite (a colourless clay mineral with fibrous habit, its ideal formula is (Mg,Al)₄Si₂O₇(OH)₂(OH₂)₄ 4H₂O) and indigo -IND-(C₁₆H₁₀N₂O₂), and the variants of IND (as dehidroindigo, the oxidized form of IND). The palygorskite is crossed by nano-tunnels, elongated in the [001] direction, filled by weakly bound zeolitic H₂O or exchangeable cations. The dimensions of these nano-channels are 6.4 × 3.7 Å. The palygorskite adsorption capacity allows it to strongly interact with organic molecules; cations and oils. The IND contains five-membered ring with carbonyl and amine functional groups, including fused benzene and palygorskite adsorption capacity allows it to strongly interact with organic molecules; cations and oils. The IND contains different chromophores, including fused benzene and five-membered ring with carbonyl and amine functional groups, along a crossed -C=C- double bond. The amazing properties of IND has been used in the fabrication of organic field effect transistors (OFETS) and its derivatives in electrochemical solar cells, dye-sensitized solar cells, electrochemical energy storage, metal corrosion inhibitors, components of fuel cells, and in artificial photosynthesis.

The importance of the Maya blue stands in its everlasting stability; the pigment is unaffected by the presence of acids, alkali, and solvents. It is also resistant to the exposure to intense light. The aim of the paper is to investigate the structural and electronic properties of the IND encapsulation within (m,m)MgONTs, with m = 5 → 8, that is, 4 NT diameters will be studied. We also investigate the exoedral NTs functionalization with the IND in two configurations: parallel and perpendicular to the MgONT surface. The paper is organized as follows: the computational details and models are presented in Sec. II, results and discussions on the structural, binding and electronic properties are presented in Sec. III, and conclusions are made in Sec. IV.

II. MODELS AND COMPUTATIONAL DETAILS

We perform first principles total energy calculations to investigate structural and electronic properties of (m,m) MgONTs to explore the encapsulation, inclusion, and adsorption of the IND using the well-established Density Functional Theory (DFT) formalism as implemented in the SIESTA code. The electron states are expanded in a linear combination of localized numerical pseudoatomic orbitals (LCAOs) using a split valence double-ζ polarized (DZP)-basis set for the valence electrons. The exchange-correlation energies are treated according to the Van der Waals density functional (VDW-DF) with the reparametrization by J. Klimes, D. R. Bowler, and A. Michaelides (KBM). The electron-ion interactions are treated within the norm-conserving pseudopotential scheme, in their fully nonlocal form. An energy cutoff of 300 Ry for the grid integration has been applied to represent the electron charge density in the real space. We consider MgONTs with chirality (m,m); m = 5, 6, 7, and 8 with diameters (D) of 8.96, 10.72, 12.52, and 14.27 Å, containing 60, 72, 84, and 96 MgO units, respectively. Infinitely, long MgONTs are described within the supercell approach using periodic boundary conditions. The supercell length along z-axis was 16.85 Å. A vacuum gap between adjacent NTs, in the lateral (x and y) directions, has been used to prevent spurious interactions. In the encapsulation and adsorption study, atoms positions of the tubes and molecule were fully relaxed until the residual forces were smaller than 0.04 eV/Å, this is following the Hellman-Feynman theorem. Brillouin-zone integrations are done using special k-points within the Monkhorst–Pack scheme. In the relaxation process, we have used a mesh of 1 × 1 × 11 and for the electronic properties (DOS, PDOS and Charge Densities) the k-points meshes were increased to 1 × 1 × 21, in all cases.

Finite size (m,m)MgONTs are modelled with supercells of different diameters depending upon the m (=5, 6, 7, 8) chiral number to investigate the inclusion process. In these cases, a vacuum gap is also taken into account along the z-direction to prevent interactions between two adjacent NTs. These open (end) NTs are terminated at one side by Mg (and at the other by O). The O terminated ends exhibit dangling bonds which are saturated with hydrogen atoms. The finite NT length is 1.14 nm. To study the composed nanostructures, we perform single point calculations at different IND parallel positions within each NT. To date, most of the peapod systems have been studied within the local density approximation (LDA) approximation therefore no dispersion corrections have been considered but it has been proved that dispersion interactions are important in these kinds of ionic peapod systems; so we consider these interactions in our studies as implemented in the VDW-DF formalism.

III. RESULTS AND DISCUSSIONS

A. Structural properties

Studies start with the structural parameters optimization, results of IND and (6,6)MgONT structures are presented in Fig. 1. In Fig. 1(a), we show the top view of the IND fragment, indicating the calculated bond lengths, C=C (1-1’), C=O(2-10), C-N(1-9), N-H(9-15), and C=O–H–N (hydrogen bond) which have values of 1.38, 1.25, 1.38, 1.03, and 2.19 Å, respectively, in good agreement with published theoretical results. The dihedral angle N-C=C-N measures 180°. In Fig. 1(b), we show the pristine relaxed MgONT structure. The Mg and O atoms are situated in the same cylindrical plane; the O-Mg and Mg-Mg (same for O-O) bonding lengths are 1.99 Å and 2.8 Å, these values are smaller than those of MgO in bulk phase, 2.11 Å and 2.99 Å. The O-Mg-O angles are 89.6°, 89.8°, 89.9°, and 90.0°, for m = 5 → 8, respectively. In the IND-(m,m)MgONTs relaxed structure, the non-covalent interactions induce slight geometrical changes on IND but large on MgONTs in all cases, both endo- and exohedral functionalization. The resulting effect is similar to...
pyramidalization in distorted SWCNTs, which can increase the reactivity in the outer wall of the MgONTs.

We now discuss the possible endohedral NTs functionalization by the IND. The first step was the analysis of the energy profile as function of the IND tilt angles measured respect to the tube axis. Results indicate that the IND molecules are close to the NT in the encapsulation case, which shows that IND molecules prefer to be tilted to make π bonding. This is similar to the molecule encapsulation in larger carbon nanotubes.29,30 Figs. 2(a) and 2(b) display the most stable configurations for the \( m = 6 \) structure. The final tilt angle is denoted by \( \theta_T \), see Table I. For \( m = 5 \), the IND O atom and NT Mg atom form an ionic bond of 2.12 Å, the tilt angle is small for small radius, and the bonding distances in the IND are larger than the original ones, which are for the C=C equal to 1.4 Å and for C=O 1.27 Å. The smallest bond between the IND H atom in the benzenes rings and the NT O (or Mg) atom is of order of 3.1 Å. For \( m = 6 \rightarrow 8 \) this value resembles that of isolated IND. The ionic forces between the NT inner wall and the IND are stronger than the π stacking when the NTs have larger radius. The average distance IND H atom–NTs O (Mg) atom is 2.43 (3.0) Å for \( m = 8 \). We calculate the distortion energy as \( \Delta E^D = E^{dist}(\text{distorted MgONTs}) - E^{dist}(\text{ideal MgONTs}) \) to examine the energetic stability and changes in the nanotubes.31 Results are \(-0.027, -0.030, -0.048, \) and \(-0.060 \text{ eV} \) for \( m = 6, 6, 7, \) and \( 8, \) respectively. This means that the clean distorted NTs are more stable than the ideal due to the reduction of symmetry as described in Ref. 15. The deformation of the MgONTs inner sidewall near the IND suggests an ionic tightly guest-host interaction.

For the exohedral functionalization, the final configurations IND-(6,6)MgONTs are depicted in Figs. 2(c)–2(f). In Figs. 2(c) and 2(d), the IND is parallel to the NT surface and there is no bonding in the IND-(6,6)MgONT system, but the organic dye is distorted with the formation of a corrugated area of the NT near the IND. In the \( m = 5 \) structure the IND O atom is attracted by the NT Mg atom inducing the O-Mg bond formation. The benzene planar shape is lost, by the presence of an O-C=C-O dihedral angle \( h_D \) with the following values: \( 166.2^\circ, 155.4^\circ, 153.7^\circ, \) and \( 153.5^\circ \) for \( m = 5, 6, 7, \) and \( 8, \) respectively. This indicates a weaker bonding and a reduced stability compared to the endohedral functionalization.

| MgONT | \( (m,m) \) | \( D \) | \( \theta_T \) | IE | \( E_{ads}(|\rangle |) \) | \( E_{ads}(|\rangle) \) | Capi |
|-------|----------|--------|---------|----|----------------|----------------|------|
| (5,5) | 8.96     | 11.2   | -2.642  | -1.806 | -1.303         | 0.426          |
| (6,6) | 10.72    | 29.5   | -4.892  | -2.347 | -3.471         | 0.264          |
| (7,7) | 12.52    | 42.7   | -4.082  | -4.185 | -4.718         | 0.120          |
| (8,8) | 14.27    | 49.6   | -4.560  | -6.223 | -6.805         | 0.090          |

FIG. 1. Ball-stick representations of the equilibrium geometry for (a) the top view of IND (b) asymmetrical view of initial (6,6)MgONT geometry. Color code: blue, white, black, red, and green represent N, H, C, O, and Mg atoms, respectively.

FIG. 2. The figure sketches the equilibrium IND molecule and the geometries of the IND-MgONT system for \( m = 6 \).
7, 8, respectively. The smallest bond length between C atoms in the IND benzene and the NT Mg (O) is 2.53(2.59) Å (see Fig. 2(c)), however for \( m = 8 \) the value increases slightly to 2.6(2.72) Å, a typical cation(anion)-π bonding of the NT Mg(O) atoms and IND C atoms.32 Meanwhile, the carbonyl and amine groups bind to atoms at the surface, in particular, the O in the carbonyl with the Mg in the NT. The -C=O bond lengths are now, 1.38, 1.39, 1.39, and 1.4 Å, for every \( m \) value, respectively, and the -C=O is 1.28 Å. The amine functional group is oriented parallel to the surface by the hydrogen bond with the NT O atom decreasing the distance and increasing the interaction.

When the IND plane is perpendicular to the MgONT surface, all H atoms align with the O atoms in the NT, in a hydrogen-like linkage. However, the O atom in the carbonyl group makes a bond with the Mg, with bond lengths of 2.01, 2.02, 2.05, and 2.13 Å, for \( m = 5 \rightarrow 8 \). The amine group also participates in the IND-(\( m,m \))MgONT bonding through the Vander Waals interaction; the IND(N-H)-NT(O) bond lengths are 1.43, 1.6, 1.45, and 1.43 Å. The IND H atom is oriented towards the NT O atom on the surface which is somewhat deformed. The relaxed structures exhibit IND O-C≡C-H dihedral angles, with values of 19.8°, 16.1°, 15.4°, and 17.5°.

For \( m = 5 \) and 7, the IND is on an oxygen row parallel to the tube z axis. In contrast for the \( m = 6 \) and 8, the IND is on a magnesium row. Finally, the calculated bond lengths IND C=O-H-N, non-interacting directly with the NT, are 2.02, 1.93, 1.93, and 1.89 Å, respectively. As the radius increases, the IND is contracted in the \( yz \) plane, see Figs. 3(e) and 3(f). The relaxed structures exhibit the O and Mg atoms alternating in adjacent rings (up-down) with a helicoidal configuration along the z-axis (see Fig. 2). The two Mg-O bond lengths are 2.04 Å and 1.94 Å in the cylindrical upper and lower planes, respectively. The Mg-O-Mg bend angle is 86.9° and the O-Mg-O bond angle is 88.2°. Finally, the radial buckling between two adjacent up and down cylindrical planes is \( \approx 0.55 \) Å; leading to NTs with a rumpled walls as the MgO(001) surface. Adjacent cations and anions alternate up and down with respect to their ideal positions (pristine MgONTs) in the perfect surface configuration.33 In fact, this is why MgONTs with chirality (\( m,m \)) are more reactive than those with chirality (\( n,0 \)) and present the pyramidalization effect. Hence, the reduction of symmetry and the minimized oxygen-oxygen electronic repulsion lead to more stable structures. The NT surface has a pattern: first, the O atoms in the same \( xy \)-plane alternate along the radial axis of the NT, in addition the O atoms in the \( z \) direction (or along the tube axis) also alternate with a similar pattern shown by the Mg atoms. However, the rumpling is more pronounced where IND is adsorbed. Without this kind of rumpling the MgONTs should be less reactive leading to physisorption.

The finite MgONT structural properties are discussed by presenting results of the IND inclusion profile in Fig. 3. The energy is plotted as function of the inclusion distance for all values of \( m = 5 \rightarrow 8 \). The abscissa measures the distance from the right edges of the composed system. According to the figure, the zero indicates that IND is totally within the NT. Results show that the electrostatic coupling is strong between the NT and IND. The main interactions take place between the NT Mg atoms and the IND O atoms of the carbonyl groups. From the initial slope of the curves in Fig. 3 at \( d \sim 15 \) Å, we may estimate the capillary force involved in the molecule insertion using the equation \( F = \Delta E/\Delta d \). The calculated values of capillarity are listed in Table I and are in good qualitative agreement with other theoretical results, based on SWCNTs.34 In our study for \( m = 6 \) \( (D = 10.72 \) Å), the capillary is 0.264 nN and the interaction distance is larger than the SWCNT in Ref. 34. Our result has been obtained taking into account an exchange-correlation functional with long-range dispersion corrections included. In the case of \( m = 5 \), the full molecule inclusion is not possible for \( d < 5 \), since the composed system needs an energy \( > 1 \) eV. When the first IND O10 atom is inside the NT and the last IND O atom is closer to the first NT Mn atom (at the edge), the ionic interaction is strong and the IND blockages the NT entrance. In practice this is somewhat difficult. For \( m = 6 \rightarrow 8 \), the insertion takes place flawlessly. In addition, at \( d = 9 \) Å the attractive force by the NTs has the maximum value, 2.021, 0.850, 0.279, and 0.135 nN for \( m = 5 \rightarrow 8 \), respectively; at this distance IND has its first benzene-ring making hydrogen bonds with O atoms in NT inner wall, see Fig. 1(a) and the inset in Fig. 3. Finally, we have obtained that for \( m = 6 \), \( \theta_0 \) takes values in the range from 0° to 35°.

### B. Intercalation and binding energies

To measure the interaction strength in the IND-(\( m,m \)) MgONTs system, we use the definition of the intercalation energy, IE, which is defined as

\[
IE = E_{\text{IND-MgONT}} - (E_{\text{MgONT}} + E_{\text{IND}}) - \Delta E_{\text{BSSE}}
\]

and the adsorption energy, \( E_{\text{ads}}(\|\perp) \) of the molecule on the MgONT surface by the formula

![Energy profile during the axial insertion of the IND molecule into the MgONTs (1-2-3-4), with the notation NT(1-2-3-4). Mg atoms terminate the MgONTs on one side, but the opposite is H saturated. The inset shows the IND entering into the (6,6) MgONT, with \( d = 9 \) Å.](image)
\[ E_{\text{ads}}(\parallel / \perp) = E_{\text{IND}}((\parallel / \perp) - \text{MgONT}) - (E_{\text{MgONT}} + E_{\text{IND}}) - \delta_{\text{BSSE}}(\parallel / \perp), \]

where \( E_{\text{MgONT-IND}} \) is the total energy of the relaxed MgONT-IND system in the encapsulation case, \( E_{\text{IND}}((\parallel / \perp) - \text{MgONT}) \) is the final energy when IND is placed parallel (\( \parallel \)) or perpendicular (\( \perp \)) at MgONT surface, \( E_{\text{MgONT}} \) and \( E_{\text{IND}} \) are the total energies of the relaxed clean MgONTs and IND in the gas phase, respectively. The Basis Set Superposition Error (BSSE) has been taken into account for corrections since we have used the Kohn-Sham orbital expansion in a set of localized atomic orbitals.\(^{35} \) With Eqs. (1) and (2) more negative energy values represent stronger interactions. It also specifies that the adsorption is exothermic, from the thermodynamical point of view.

In all cases, IND is chemisorbed within and on the NT surface as indicated by the IE and Eads values reported in Table I. In each case, we obtain negative values smaller than \(-1 \text{ eV}\) indicating that the composed systems are energetically more stable than the isolated constituents, we conclude that reactions are exothermic. Note that for the \( m = 5 \) the three cases: encapsulation, parallel, and perpendicular adsorption have lowest binding energies. For the encapsulation, when \( m = 6 \), the organic-ionic peapod has the maximum coupling energy \(-4.892 \text{ eV}\). When \( m > 6 \) the coupling energy decreases. Based on these results and the profile energy in Fig. 3, we conclude that the nanotube with \( m = 6 \) \((D = 10.72 \text{ Å})\) is the one that offers the best conditions for the IND encapsulation. On the other hand, the IND adsorption in the parallel or perpendicular configurations to the surface exhibit also large adsorption energies. When the organic dye is parallel to the NT surface, the functionalized system exhibits a binding energy monotonic increase which is a consequence of the large area covered by the IND on the NT surface. In contrast, no equivalent behaviour is observed in the perpendicular adsorption since the absolute energy difference when \( m = 6 \) and \( m = 5 \) is \(-2.17 \text{ eV}\). For \( m = 7 \) and \( m = 6 \), the energy difference is \(-1.25 \text{ eV}\) and for \( m = 8 \) and \( m = 7 \), it is \(-2.08 \text{ eV}\). The aforementioned shows the existence of selective interaction sites, examples are indicated by the arrows of the O atoms. When the IND is parallel to the NT surface the effective contact area is maximized resulting in large binding energies. However, the atomic correlation between IND and the NT sidewall (see Figs. 4(c) and 4(d)) yield larger binding energy in the perpendicular configuration where the atoms in the IND edge are well aligned in the direction of NT O atoms, see Figs. 4(e) and 4(f). Our results are in good qualitative agreement with those recently reported.\(^{36} \)

The experimental results of metal oxide polar surfaces interacting with benzene and phenoxy also support our findings reported in Secs. III A and III B.\(^{37} \) The calculated energy values are significantly larger than those of carbon nanopeapods in good agreement with those of the ionic-peapod, see Ref. 27. Note that our calculations have been done using the VDW-DF theory. Recall that the corresponding LDA approach overestimates binding energies, while the generalized gradient approximation (GGA) formalism underestimates these energies.

C. Charge transfer characteristic

An important property of the NT-IND system is the charge transfer. The charge density difference (CDD) is defined as

\[ \Delta \rho(r) = \rho_{\text{IND-MgONT}}(r) - (\rho_{\text{MgONT}}(r) + \rho_{\text{IND}}(r)). \]  

In Eq. (3), \( \rho_{\text{IND-MgONT}} \), \( \rho_{\text{MgONT}} \), and \( \rho_{\text{IND}} \) are the charge densities of the IND-MgONT structure, MgONT, and the isolated IND molecule, respectively. Recall that the charge density includes only the valence electrons. As a representative example, Figs. 4(a)–4(f) show the nanohybrid system with \( m = 6 \) in the three configurations. In the plots, the blue (white) colour indicates the area where there is depletion (accumulation) of electron charge density. It is evident from the 3D CDD plot that the electron charge density distribution has changed significantly. Figs. 4(a) and 4(b) show charge redistribution located at one side of the IND, which produces the indoxyl polarization meanwhile the other side remains unchanged. In a similar fashion, the NT displays electronic charge on the outer surface in the normal direction where the indoxyl is polarized. The H-chromophore plays an important role in the encapsulation due to the charge depletion in the N-H (electron donor) bond.
and the charge increase in the -C=O (acceptor) groups, see Fig. 4(b). The non IND-(6,6)MgONT charge overlap means non-covalent interactions and a strong charge transfer in the sub-systems from the IND C atoms to the NT O atoms because of the larger O electronegativity than those of C and N. The IND C atoms and the amine groups in the H-chromophore are expected to yield electrons to the atomic tube. As a result of this charge transfer, IND is oxidized.

The parallel and perpendicular configurations (Figs. 4(c)–4(f)) are fully polarized and the electronic charge is distributed in the normal direction to the IND benzene plane. Figures 4(d) and 2(c) (4(f) and 2(e)) show sections of the NTs, where the IND is adsorbed with the buckling height being maximal, however the electron charge is located far from the dye with certain polarizability only in the NT. The anti-bonding contribution of C p orbitals and O p orbitals is present, the repulsion polarizes the IND π-cloud giving rise to an attractive interaction by the Mg cations and O anions, which can be considered as a polarization state.38

The host system is composed of O and Mg (an alkaline earth metal cation with oxidation number +2), which enhances the strength of the ion-π bonding in the ionic-organic nanopaprod.39 The electron charge redistribution in the parallel configuration induces a more stable geometry than that of the perpendicular structure. This is due to the fact that the carbon atom sp² hybrid orbital cannot overlap with any surface states, thus the ionic coupling IND O–NT Mg and the CH-π interaction are stronger than those in the parallel adsorption.

The charge transfer and redistribution are related to the ionicity and polarizability. The Voronoi deformation density (VDD) method40 was adopted to analyse the charge distribution integrating the CDD, Eq. (3). The VDD method is not basis dependent as Mulliken population analysis. We also find that this VDD approach yields more reliable results.

We calculate the charge deformation produced by the bonding between the MgONT and the IND molecule using the formula

\[
\Delta Q_A = \int_{Voronoi\ cell\ A} \left[ \rho_{IND-MgONT}(r) - (\rho_{MgONT}(r) + \rho_{IND}(r)) \right] \mathrm{d}r.
\]

The IND-(m,m)MgONT bonding is mainly mediated by the strong ion-π interaction between the NT Mg rows and the IND O atoms in the carbonyl groups, in agreement with calculations which reveal a large charge transfer from the IND to the NT.

The total charge transfer from the IND to the NT is reported in Table II, considering the initial configuration as the reference. Table II shows that the largest charge transfer takes place in two main configurations, the first is when IND is encapsulated and the second when IND is parallel adsorbed. Charge transfer has values greater than 0.5e, provided that the IND may cover large area on the NT oxygen atoms. In the perpendicular configuration, the charge is transferred from the IND carbonyl O atom (labelled O10 in Fig. 1(a) and in Table II) to the nearest Mg atom at the NT surface. The charge transfer from IND to NTs is lowered in all cases for \( m > 5 \). \( m = 5 \) is a special case, the encapsulation has the maximum electron charge transfer, as a result of the 1D strong confinement by the small NT diameter and because of the electronegativity of the O which is greater than those of C and N. The column labelled Ads(∥) and Ads(⊥) show the same behavior as the binding energies in Table I. As a result, the C and N atoms are more likely to free electrons.

According to the results presented above, we conclude that the large binding energies are polarizability induced (by the ion-π interactions) in addition to the high surface reactivity due to the buckling effect in the NTs. Mainly, the atomic correlation and the large cover area by IND in the encapsulation and the parallel adsorption lead to cation(anion)-π interaction in the Mg(O)-C bonding, which explains the resulting short bond lengths and the very strong binding strength reported in Secs. III A and III B. The aforementioned features should induce substantial changes in the electronic structure of the composed system, as discussed below.

D. Electronic properties

1. Total density of states and partial density of states

The IND-(m,m)MgONT total density of states (DOS) and partial density of states (PDOS) are described in this section. Fig. 5(a) shows the total IND DOS near the Fermi level, indicating the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In all cases, the main absorption is originated by the HOMO($S_0 \rightarrow LUMO$) transitions. Experimentally, this has energy of 2.3 eV.41 The calculated energy gap between the HOMO ($S_0 \rightarrow LUMO$) and LUMO ($S_0 \rightarrow S_1$) transitions is 1.32 eV. The charge distribution is reported in Figs. 6(a) and 6(b). The molecule π and π* bonds, and O and N p orbitals make the major contribution to the HOMO and LUMO.

The total DOS of the (6,6)MgONT is plotted in Fig. 5(b). The effects of the 1D confinement are manifested

| MgonT (m,m) | I | Ads(∥) | Ads(⊥) | O10(|I|) | O10[Ads(∥)] | O10[Ads(⊥)] | Mg[∥] |
|------------|---|--------|--------|---------|-------------|-------------|-------|
| (5,5)      | 1.362 | 0.699 | 0.101 | 0.136 | 0.137 | 0.027 | 0.015 | 0.084 | 0.015 | −0.103 | −0.105 | −0.080 |
| (6,6)      | 1.256 | 0.744 | 0.260 | 0.111 | 0.113 | 0.032 | 0.047 | 0.121 | 0.018 | −0.117 | −0.129 | −0.101 |
| (7,7)      | 0.973 | 0.763 | 0.105 | 0.077 | 0.041 | 0.036 | 0.056 | 0.093 | 0.019 | −0.100 | −0.092 | −0.08 |
| (8,8)      | 0.686 | 0.786 | 0.212 | 0.005 | 0.003 | 0.031 | 0.076 | 0.127 | 0.02 | −0.079 | −0.072 | −0.098 |
in the conduction band by small singularities in the vicinity of 0 eV in the NTs. The clean NT energy bandgap $E_g(\text{clean})$ shows convergence with the radius to resemble the MgO monolayer bandgap, this result is in agreement with that of Ref. 15. The electronic properties change with the encapsulation or adsorption. The IND-(m,m)MgONT DOS in both endohedral and exohedral functionalization differs from the simple superposition of its components.

Results reported in Table III indicate that the IND encapsulation within the MgONT, the structure with $m = 5$ has an energy bandgap $E_g(C)$ larger than those of $m = 6, 7$ structures, however smaller than the $m = 8$ structure. For $m = 6$, the hybrid system is a semiconductor with $E_g(C) = 0.27$ eV. For $m \geq 5$ in the parallel adsorption the bandgap $E_g(\|)$ increases monotonically similar to the $E_{\text{ads}}(\|)$ behaviour, see Table I. The last column in Table III the $E_g(\perp)$ increases as $E_{\text{ads}}(\perp)$ increases, Table I. For $m = 5$ and 7, in the perpendicular configuration, the IND adsorption final position was on top of the Mg atoms, and for $m = 6$ and 8, the adsorption was on the O atoms.

In every case, the LUMO of IND and the HOMO of MgONT form the HOMO-LUMO bands of the IND-(m,m)MgONT structure, see Figs. 6(d), 6(f), 6(h) and Figs. 6(c), 6(e), 6(g). It is clear that the composed system displays a semiconductor character because of the endo/exohedral NT functionalization by the IND. The Fermi level shifts to lower which is accompanied by the charge transfer from the IND C and N $\pi$ orbitals to the O $p$ orbital in the NT lattice. This may be corroborated in the total and projected DOS shown in Figs. 5(c)–5(h) and Fig. 6(c), where the valence band in the three cases is of the MgONTs O 2p states and Mg 3s states. From the PDOS plot, it can be seen that the bottom of the conduction band has a C and N 2p character. In the perpendicular adsorption, note the presence of sharp peaks around 6 eV, of the N and C 2p states are associated with the non-interacting IND atoms near the (m,m)MgONT surface, thus the electronic charge of these N and C is unaffected. We conclude that the main process in the parallel adsorption is related to ion-$\pi$ interactions of the Mg cation and O anion with the oxidized benzene rings. On the other hand, the atomic contribution from Mg to any molecular orbital is very small (the orbital interaction between Mg cations and IND is not important); however the O contribution is significant as sketched by the electron charge redistribution. The remarkable dispersion of the IND C p orbitals in the valence band is due to the overlapping with the NT O p orbitals, which is compensated by antibonding states. As a result of the IND-polarized NT interaction there is a drastic reduction of the bandgap. This last effect takes place when the IND interacts with polar solvents.

2. Electric dipole moment

The clean MgONTs exhibit no electric dipole moment (EDM in Debye). Since the (m,m)MgONTs are ionic compounds the positive charge equals the negative charge in the
The hybrid system shows an increase in the polarizability when the excess of electron charge is on the NTs. The hybrid-structure is unrealistic according to the energy profile in Fig. 3. This is similar to the terthiophene within the zigzag carbon nanotubes and explained by Dumitrica et al. When the nanopeapod has chiralities > 5, the EDMs increase with the direction along the IND O-O bond on the xy-plane, see Fig. 4(b).

Finally, in the perpendicular adsorption the EDMs is normal to the IND benzene-plane; however there is an EDM component directed from IND to MgONTs which grows as D increases.

### IV. CONCLUSIONS

We have reported studies on the structural and electronic properties of the \((m,m)\)MgONT functionalized by the IND dye. It has been studied the IND encapsulation, adsorption, and inclusion in NTs with \((m,m)\) chirality; \(m = 5, 6, 7, \) and 8. The encapsulation and parallel adsorption process show non-covalent interaction with strong binding energies and short bond lengths which indicate chemical bonding. When IND is chemisorbed on the NT, the binding energies increase with the \(m\) index by cation-\(\pi\) interactions due to Mg and anion-\(\pi\) interactions by the O. In the inclusion process, a potential barrier is found which diminishes as the \(m\) index increases. The IND-(\(m,m\))MgONT interactions are accompanied by a substantial charge transference from the IND to the NTs induced by the high electronegativity of the oxygen atoms in the NTs. The atomic correlation factor is dominant over the effective contact area favoring the perpendicular adsorption (not ion-\(\pi\) bond). The main contributions are made by the C and N p orbitals, which indicate that the IND acts as a charge donor, consequently a charge-transfer “ion-\(\pi\)” complex model is proposed as the mechanism. In addition, the interactions affect the structural and electronic properties of both the IND (slightly) and the NT (strongly) yielding rippled NTs with high reactive exterior surface accompanied of preferential adsorption sites which facilitates sidewall decoration. Thus, the structural properties of IND are retained however the full system is accompanied of new unusual electronic properties. The HOMO levels in each case show that the electronic charge is localized on the NT surface away from IND, and in the LUMO level the charge distribution is on the IND. As a result, the polarization is induced with the electric dipole moment pointing in the normal direction to the benzene plane, in the parallel adsorption. The electronic properties of IND-(\(m,m\))MgONTs are sensitive to the 1D confinement as a result it is obtained semiconductors with narrow band gaps. The small energy gaps induced by the noncovalent functionalization of MgONTs make this hybrid system a good candidate for new nanomaterials and the design of novel nanostructures. Finally, the long-range

**TABLE III.** Bandgap when MgONTs are clean \(E_g\)(clean), with IND is inside the NTs \(E_g\)(C), and when IND is adsorbed parallel \((\parallel)\) and perpendicular \((\perp)\) on the NTs surface in eV/molecule.

<table>
<thead>
<tr>
<th>MgONT ((m,m))</th>
<th>(E_g)(clean)</th>
<th>(E_g)(C)</th>
<th>(E_g)((\parallel))</th>
<th>(E_g)((\perp))</th>
</tr>
</thead>
<tbody>
<tr>
<td>((5,5))</td>
<td>3.93</td>
<td>0.60</td>
<td>0.66</td>
<td>0.96</td>
</tr>
<tr>
<td>((6,6))</td>
<td>4.05</td>
<td>0.27</td>
<td>0.66</td>
<td>0.81</td>
</tr>
<tr>
<td>((7,7))</td>
<td>4.08</td>
<td>0.51</td>
<td>0.72</td>
<td>1.06</td>
</tr>
<tr>
<td>((8,8))</td>
<td>4.17</td>
<td>0.69</td>
<td>0.75</td>
<td>0.90</td>
</tr>
</tbody>
</table>

**FIG. 6.** Isosurface charge densities at the \(\Gamma\)-point, for the HOMO and LUMO states in the hybrid systems IND-MgONTs, with \(m = 6\). The isovalue is 0.05 a.u.
dispersion corrections in the exchange-correlation functional are important in the description and stabilization of this kind of organic-ionic complex structures.

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