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«HOST-GUEST» COMPLEXING OF DOUBLE-WALLED CARBON NANOTUBE WITH METALLOCENES

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Complex compounds of various types and nature have been widely applied in many fields of science and technology. Complex aggregates based on nanostructures such as nanotubes and other coordination compounds, for example, metallocenes, have unique properties, since a combination of their individual characteristics provides for further growing interest to the research in chemistry, physics, electronics, medicine, etc.

The initial structure was a (5.5)@(10.10) nanotube (CNT) having 270 carbon atoms. Intercalation of this double-walled carbon nanotubes (DWCNT) assumes placing the intercalate inside the (5.5) CNT, into intertubular space, and its differently oriented sorption on the outer surface of the (10.10) CNT.

By employing the methods of MM+, PM3 and Monte-Carlo, the positioning has been studied of molecules of tricarbonyl(cyclopentadienyl)manganese, monocyclopentadienylferrum(II), bis(cyclopentadienyl)nickel and bis(η^5-cyclopentadienyl)cobalt in a double-walled (5,5)@(10,10) carbon nanotube depending on intercalate concentration and intercalation temperature. The temperature increase (over ~455–460 K) causes gradual bond ruining followed by extrusion of interwall intercalate. Further temperature increase up to 620–650 K is characterised with intercalate external surface desorption, stabilising the whole systems and keeping the interwall intercalate only.

It is necessary to note that the suggested model variant allows to demonstrate the thermodynamic selectivity of physical and chemical sorption-desorption. At lower temperatures there appears physical sorption, its natural feature is most likely to overlap the non-hybridized orbital $3d_{xy}$ of the metal ions with the π-system of the DWCNT side surface while chemisorption is observed at higher temperatures that is peculiar or π-π interactions of aromatic and quasiaromatic cyclic (heterocyclic) systems.

Moreover, simultaneous presence of donor/acceptor feature of the DWCNT's intertube space as a result of positive and negative Gaussian curvature, makes it possible to regulate orientation of intercalate donor and acceptor edges what allows us to view it as a potential molecular switch.

There have been calculated the UV-spectra for (5,5)@(10,10) DWCNT depending on the intercalate concentration as well as an association constant of the systems which makes 26.45 $l\cdot mol^{-1}$ (for system with ferrocene); 36.2 $l\cdot mol^{-1}$ (for system with nickelocene); 76.8 $l\cdot mol^{-1}$ (for system with cobaltocene) and 6.745 $l\cdot mol^{-1}$ (for system with manganocene).

Keywords: *intercalation, double-walled carbon nanotube, "host-guest" complex tricarbonyl(cyclopentadienyl)manganese, monocyclopentadienylferrum(II), bis(cyclopentadienyl)nickel, bis(η^5-cyclopentadienyl)cobalt*

INTRODUCTION

Unique physical properties of multi-walled nanosystems (especially of graphene-based ones) have been the subject of keen interest lately. Their specific energy-band structure with a zero band gap and linear dependence of electron and hole energy spectrum on the wave-vector cause the electric charges to behave like relativist particles with zero effective mass [1–3]. Anomalous transportation and field effects open a wide prospect of their applying in nanoelectronics [4–7]. Such nanostructures are assumed to be promising spintronics materials due to the long electron free path, weak spin-orbital interaction and the long spin scattering [8, 9]. What is more, the chemical or physical modification of multi-walled nanosystems enables to reveal their new extraordinary features. Thus, intercalation with atoms (molecules) allows to change the Fermi level position, relative electron and hole concentration, without considerable changes in energy-band structure of source nanomaterials [10–12].

On the other hand, unique optical, electrical and magnetic, and also biological behaviour of cyclopentadienyl complexes [13, 17–21] stimulate creation on their base of intercalates with multi-walled CNT (MWCNT), since the capability of these complexes to coordinate with MWCNT [6, 10, 19–21] allows to obtain new materials as effective elements for photo- and magnetosensitive devices, drug delivery, imaging and therapy, as well to use these materials as an antidetonant in motor and aviation fuels.

As identification of structure-to-property relations is an important task of chemistry and materials physics, the aim of this work was to study the structure of intercalated metallocenes, such as tricarbonyl(cyclopentadienyl)manganese, monocyclo-pentadienylferrum(II), *bis*(cyclopentadienyl)nickel and *bis*(η^5-cyclopentadienyl)cobalt, double-walled CNT (DWCNT) when heating by the methods of MM+, PM3 and Monte-Carlo, to calculate the UV-spectra of a DWCNT depending on intercalate concentration as well as to determine the association constant of the "DWCNT-intercalate" system.

MODEL AND METHODS

The initial structure was a (5.5)@(10.10) CNT having 270 carbon atoms. Intercalation of this DWCNT assumes placing the intercalate inside the (5.5) CNT, into intertubular space, and its differently oriented sorption on the outer surface of the (10.10) CNT.

The intercalate are the tricarbonyl(cyclopentadienyl)manganese, monocyclopentadienylferrum (II), *bis*(cyclopentadienyl)nickel and *bis*(η^5-cyclopentadienyl)cobalt molecules (Fig. 1).

a *b* *c* *d*

Fig. 1. The molecules as the intercalate: *a* – tricarbonyl(cyclopentadienyl)manganese; *b* – monocyclopentadienylferrum(II); *c* – *bis*(cyclopentadienyl)nickel; *d* – *bis*(η^5-cyclopentadienyl)cobalt

It is their relative position, orientation relatively the CNT walls, behaviour in the intertubular space and the system as a whole, as well as the quantitative characteristics of bonding with the DWCNT at temperature change what is the subject of this calculation.

In the model considered the interaction potential (Leonard-Jones potential) between metal ions (see Eq. (1)) and a cyclopentadienyl anion directly mated the pair potential of high energy of atomic excitation [14] and it was described by the Born-Mayer equation within 0–0.68 nm of effective interaction radius (see Eq. (2))

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \qquad (1)$$

where r – distance between particle centres, ε – depth of potential pit, σ – distance at which the interaction energy is equal to zero (parameters ε and σ characterise atoms of corresponding substances);

$$U(r) = A\exp(-r/b), \qquad (2)$$

where A, b – constant, for every pair of colliding particles, r – distance between interacting particles.

To describe the atom interaction at a distance smaller than 0.2 nm, we have used the Tersoff-Brenner potential of interatomic interaction [15]. Total potential energy of system U is expressed as a sum of bonding energies for all pairs of atoms forming this system

$$U = \sum_{i} \sum_{j>i} \left[V_R\left(r_{ij}\right) - B_{ij}^{*} V_R\left(r_{ij}\right) \right], \qquad (3)$$

where *rij* – distance between i and j atoms; $V_R(r)$ and $V_R(r)$ – exponential functions included into the Morse potential type which corresponds to the energies of attraction and repulsion between the atoms; *Bij** – the function expressing the dependence of binding energy of the *i* and *j* atoms on the angles θ_{ijk} between the bond *i-j* and close bonds *i-k* and *j-k*.

To describe the atom interaction at a distance greater than 0.21 nm we have employed the Tersoff-Brenner potential of interatomic interaction [15] along with the Ziegler-Biersack-Litmark pair potential [14]. The length of C–C bonds in a CNT was 0.139 nm, the metal–C interaction was described by the Lennard-Jones pair potential [16] with potential interaction energy 0.12 eV. The modelled period of one excitation cascade was 2 ps, and the energy conservation law in every calculation cycle was correlated within 0.15 %. The initial coordinates of the intercalate were selected in conformity with the law of random numbers.

To do the task above the following numerical modelling scheme was used:

1) the first calculation stage was based on the MM+ molecular mechanics method;

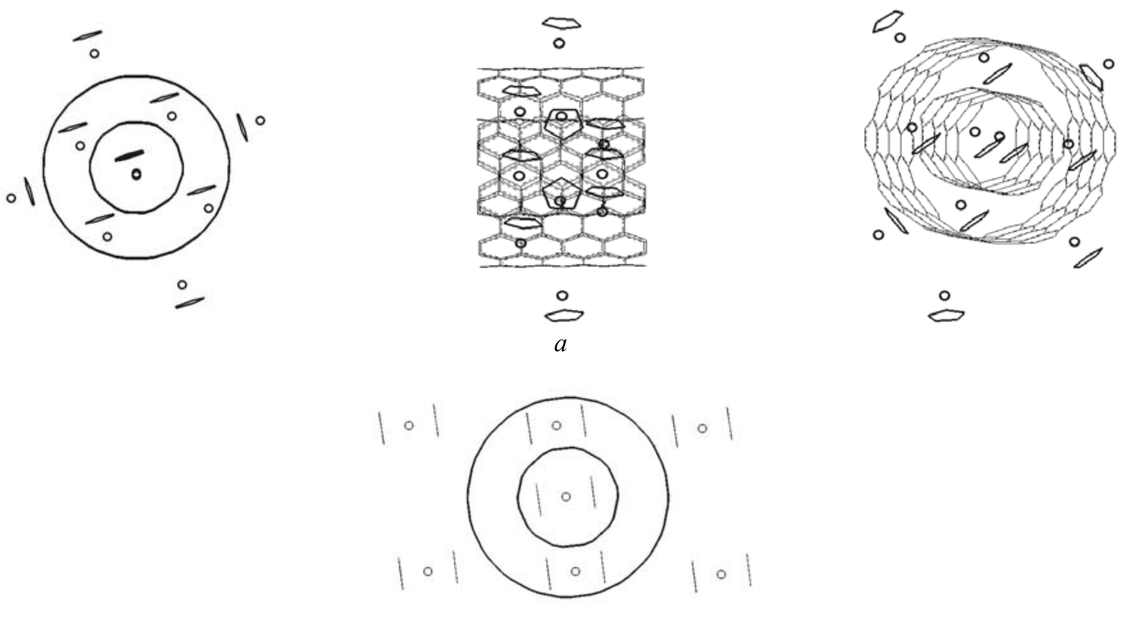
2) the second stage was based on the semi-empirical PM3 method. It should be noted that the main distinction of this method from the others is their different parameterisation. In our case the PM3 method was reparameterised to the best match of calculated and experimental molecule formation heats;

3) the third stage was based on the Monte-Carlo method.

To calculate the association constant of the "DWCNT-intercalate" complex formed, there has been employed the modified Benes-Hilderbrand method [17] that accounts the data on maximum DWCNT absorption values at various intercalate concentrations in the UV-spectra.

RESULTS AND DISCUSSION

All the systems studied (see Fig. 2) proved to be rather heat-resistant in a wide temperature range (up to ~900 K). At that the deformation vibrations of the DWCNT crystal grate do not exceed 0.015 nm, and the vibrations of the intercalate molecules do not exceed 0.025 nm that provides for configuration and conformation stability of the system.



a

b

Fig. 2. Starting a geometric model of the "DWCNT-intercalate" system (the orthogonal projections and a side-view): *a* – manganocene and ferrocene structures with DWCNT; *b* – nickelocene and cobaltocene structures with DWCNT

Temperature dependence of the all model systems energy is shown in Fig. 3. As it is seen, when initially heated from 273 to ~460 K, the systems energy grows gradually, then rises sharply between 460–490 K and 750–760 K, then, with temperature growth, it reaches the plateau what proves its high stability up to ~920 K. These temperature ranges are almost the same for all model systems with different intercalates.

The modelling performed allows us to determine the following dynamics of the intercalated DWCNT structures when heated: when initially heated to ~455–460 K, all the systems remain rather stable, there is no extrusion of the intercalate molecules. Vibrational and rotational (along the quintic axis) capabilities of bonds and angles of DWCNT and metallocene molecules are observed. When the system temperature is increased to ~455–480 K, rapid intercalate extrusion out of the intertube space of all the systems appears. At the temperature of ~740–760 K, there is observed desorption from the outer surface, except for only two intercalate molecules being ferrum-oriented to the CNT wall. At the temperature of over ~900 K there appears full external desorption while the inner (5.5) CNT remains completely filled (Fig. 4 shows the screenshot of configurational change of the “DWCNT-intercalate” systems when heated).

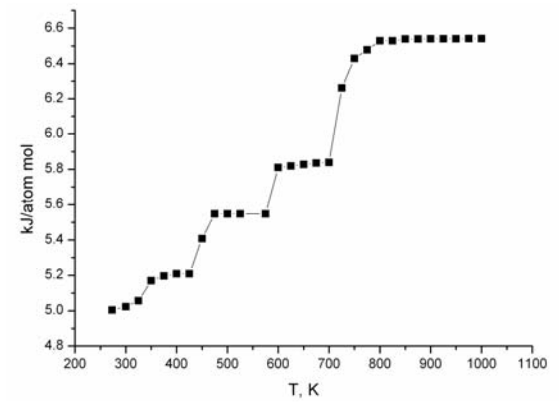
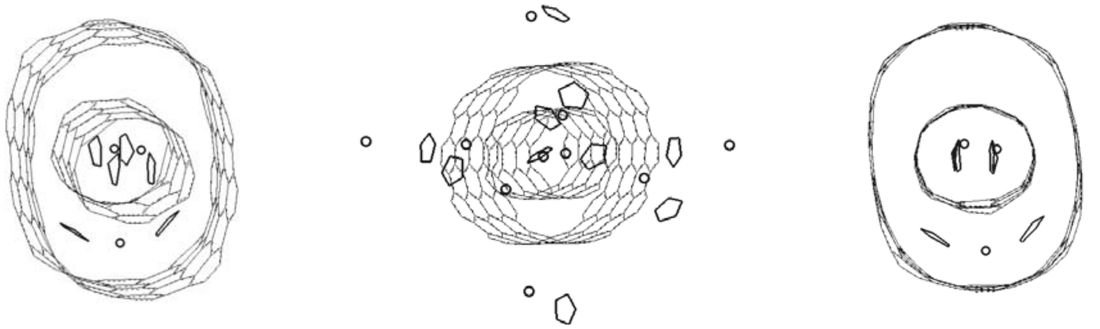


Fig. 3. Temperature dependence of the “DWCNT-intercalate” model systems



a *b* *c*

Fig. 4. Screenshot of configurational change of the “DWCNT-intercalate” systems under heating: *a* – tricarbonyl(cyclopentadienyl)manganese structure; *b* – monocyclopentadienylferrum(II) structure; *c* – *bis*(cyclopentadienyl)nickel and *bis*(η^5-cyclopentadienyl)cobalt structures

It should be noted that this variant of the model suggested allows us to demonstrate the thermodynamic selectivity of physical and chemical sorption-desorption. Within the temperature range 273–460 K physical sorption appears, its natural feature is most likely to overlap the non-hybridized orbital $3d_{xy}$ of the metal ions with the π-system of the DWCNT side surface while chemisorption is observed at higher temperature values (~600 K) that is peculiar of π-π interactions of aromatic and quasiaromatic cyclic and heterocyclic systems.

Moreover, simultaneous presence of donor/acceptor feature of the DWCNT’s intertube space as a result of positive and negative Gaussian curvature, makes it possible to regulate orientation of the intercalate donor and acceptor edges what allows us to view it as a potential molecular switch.

Finally, theoretical calculations of UV-absorption spectra of the (5.5)@(10.10) CNT depending on the intercalate concentration in terms of the modified Benes-Hilderbrand method shows that the association constant of the system studied is 26.45 $\text{l}\cdot\text{mol}^{-1}$ (for system with ferrocene), 36.2 l·mol^{-1} (for system with nickelocene), 76.8 l·mol^{-1} (for system with cobaltocene) and 6.745 l·mol^{-1} (for system with manganocene). In all cases the correlation coefficient was $R \geq 0.99$.

CONCLUSION

The type of metallocene molecules arrangement on the outer side surface, on the inner surface as well as in the intertube space of the (5,5)@(10,10) DWCNT has been found. The calculations made allow to prove discover that the "DWCNT-intercalate" system is rather stable at high temperature (up to ~455 K) that provides reliability and stability of the process of intercalate synthesis under conditions regular for this procedure. However, at further heating the gradual intercalate extrusion out of the intertube space, intercalate outer surface desorption (at the temperature 700–750 K) as well as thermodynamic stabilisation of the system containing the intertube intercalate only are observed. The association constant of the "DWCNT-intercalate" system has been theoretically calculated to be equal to 26.45 l·mol^{-1} (for system with ferrocene), 36.2 l·mol^{-1} (for system with nickelocene), 76.8 l·mol^{-1} (for system with cobaltocene) and 6.745 l·mol^{-1} (for system with manganocene).

Комплексоутворення між двошаровими карбоновими нанотрубками та металоценами за типом «гість-хазяїн»

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З використанням методів молекулярної механіки ММ+, напівемпіричного квантово-хімічного РМ3 та Monte-Carlo досліджено характер розташування молекул металоценів у двошаровій (5,5)@(10,10) карбоновій нанотрубці (ДКНТ) залежно від концентрації інтеркалянту і температури інтеркалювання. Зі зростанням температури (понад ~455–460 K) відбувається поступове руйнування утворених зв'язків з екструзією міжтрубного інтеркалянту. Подальше підвищення температури до 620–650 K характеризується зовнішньоповерхневою десорбцією інтеркалянту та врешті-решт стабілізує досліджувану наносистему загалом, зберігаючи лише внутрішньотрубний інтеркалят. Розраховано УФ-спектри (5,5)@(10,10) ДКНТ залежно від концентрації інтеркалянту та визначено константи асоціації систем, що становлять: 26.45 л·моль$^{-1}$ (для системи з фероценом); 36.2 л·моль$^{-1}$ (для системи з нікелоценом); 76.8 л·моль$^{-1}$ (для системи з кобальтоценом) та 6.745 л·моль$^{-1}$ (для системи з манганоценом).

Ключові слова: *інтеркалювання, двошарова карбонова нанотрубка, комплекс типу «гість-хазяїн», біс(циклопентадієніл)манган, моноциклопентадієнілферрум(II), біс(циклопентадієніл)нікель, біс(η^5-циклопентадієніл)кобальт*

Комплексообразование между двухслойными углеродными нанотрубками и металлоценами по типу «гость-хозяин»

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Используя методы молекулярной механики ММ+, полуэмпирический квантово-химический РМ3 и Monte-Carlo, исследован характер размещения молекул металлоценов в двухслойной (5,5)@(10,10) углеродной нанотрубке (ДУНТ) в зависимости от концентрации интеркалята и температуры интеркалирования. С увеличением температуры (выше ~455–460 K) происходит последовательное разрушение образованных связей с экструзией межтрубного интеркалята. Последующее увеличение температуры до 620–650 K характеризуется внешнеповерхностной десорбцией интеркалята и стабилизирует исследованную систему в целом, сохраняя при этом только внутритрубный интеркалят. Рассчитаны УФ-спектры (5,5)@(10,10) ДУНТ в зависимости от концентрации интеркалята и найдены константы ассоциации систем, которые *составляют: 26.45 л·моль$^{-1}$ (для системы с ферроценом); 36.2 л·моль$^{-1}$ (для системы с никелоценом); 76.8 л·моль$^{-1}$ (для системы с кобальтоценом) и 6.745 л·моль$^{-1}$ (для системы с манганоценом).*

***Ключевые слова:** интеркалирование, двухслойная углеродная нанотрубка, комплекс типа «гость-хозяин», бис(циклопентадиенил)марганец, моноциклопентадиенилжелезо(II), бис(циклопентадиенил)никель, бис(η^5-циклопентадиенил)кобальт*

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