PECULARITIES OF POLYNUCLEOTIDES WRAPPED AROUND CARBON NANOTUBES: MOLECULAR DYNAMICS MODELING AND SPECTROSCOPY STUDY

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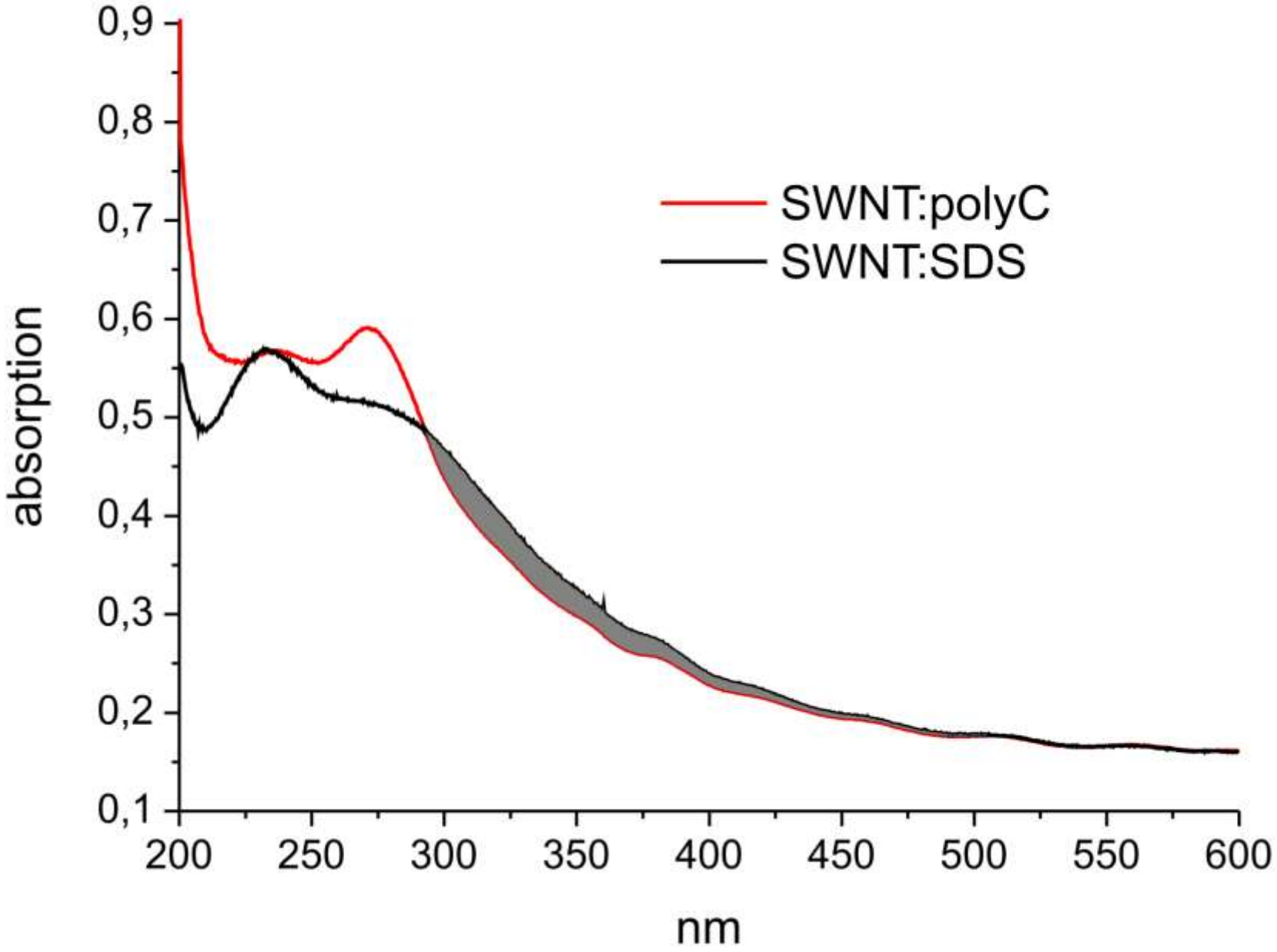
purposes of our study

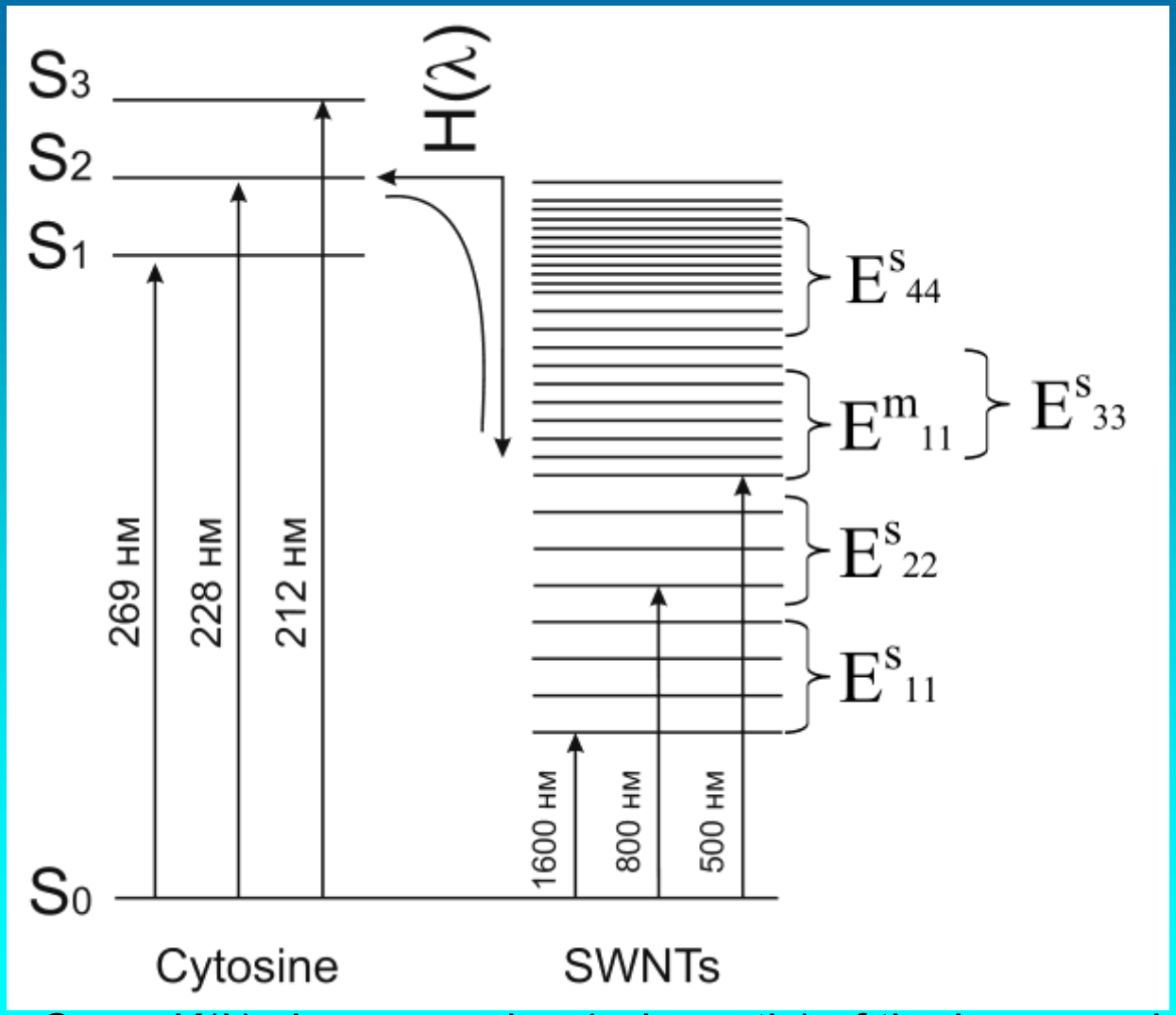
One the purpose of our study was an analysis of adsorption on the carbon nanotubes surface of the two polymers: poly(rC) and poly(rG) with the different base structure.

π-π stacking interaction between the nanotube and π-conjugated nitrogen bases

- Due to its helical structure, DNA or RNA can wrap tightly around the nanotube in water spontaneously. The quantum-chemical calculation confirms that π-π stacking between nitrogen bases and the nanotube surface is the basic mechanism of SWCNT:DNA interaction and the major reason of the hybrid stability.
- The π-π stacking interaction between the nanotube and π-conjugated nitrogen bases manifested directly in transformation of DNA absorption spectrum and can be also observed in the absorption spectrum of polymer-wrapped nanotubes. Polynucleotide interaction with carbon nanotubes induces decrease of carbon nanotube absorption intensity (hypochromicity effect) in 300-400 nm region in comparison with absorption of SWNT covered with such surfactant as sodium dodecyl sulfate (shortly SDS) which has no π-conjugated system.

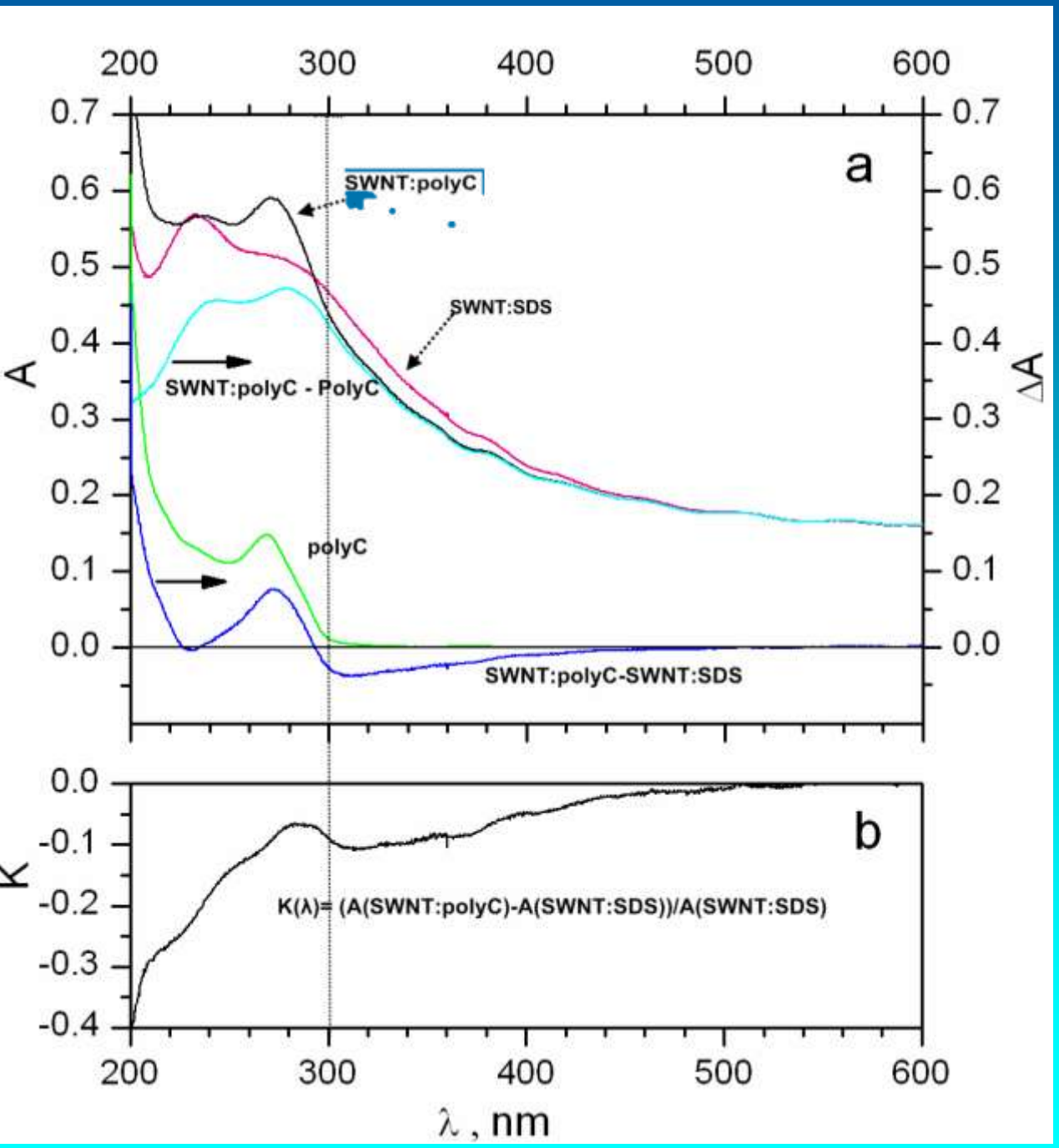

0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
absorption
200
250
300
350
400
450
500
550
600
nm
SWNT:polyC
SWNT:SDS

arrangement of electronic levels of cytosine and SWNT



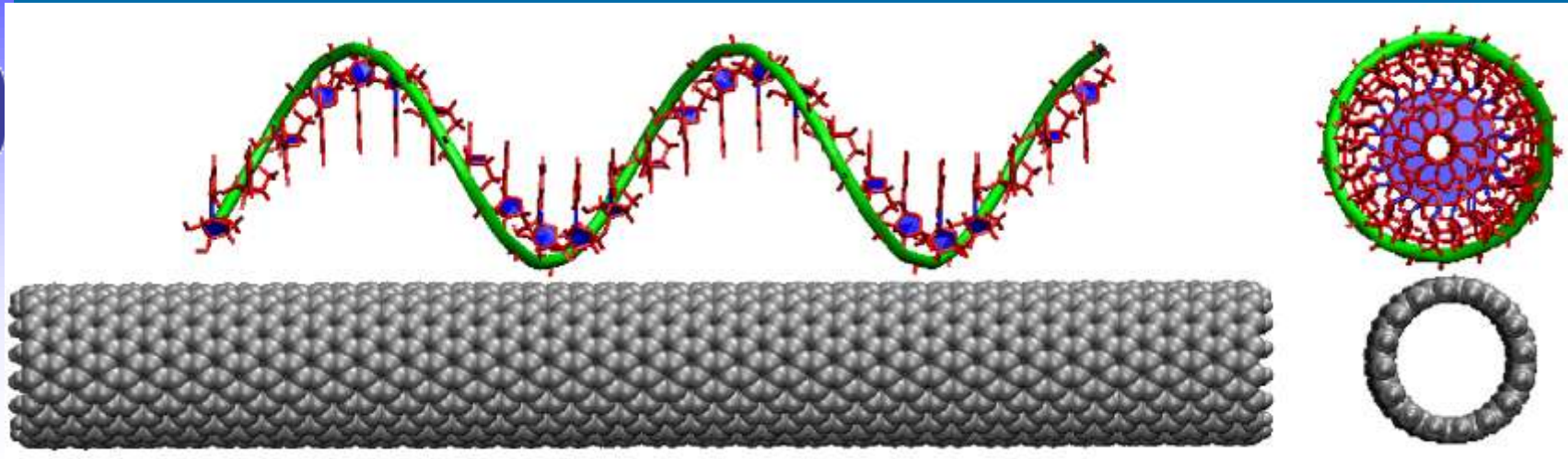
When analyzing Table with electronic transitions of HiPCO nanotubes [R. Bruce Weisman and Sergei M. Bachilo, Nano Lett. 3(9), 1235-39 (2003)] we found 22 bands in the 300-400 nm range, induced by E_{33} and E_{44} transitions in semiconducting nanotubes of different chirality and diameters (from 0.75 to 1.2 nm). As well, in 350-300 nm range absorption bands, caused by E_{22} transition in metallic nanotubes should also appear.

Curve K(λ) shows growing (schematic) of the hypocromic effect as energy levels of nanotubes are approached towards cytosine singlet levels.



UV-vis absorption spectroscopy determination of SWCNTs hypochromism: SWNTs:poly(C)

The initial configuration of the complexes SWCNT with gomooligonucleotides $r(I)_{25}$ and $r(C)_{25}$



Biopolymers: $r(C)_{25}$, $r(G)_{25}$

Biopolymers length – 25 bases

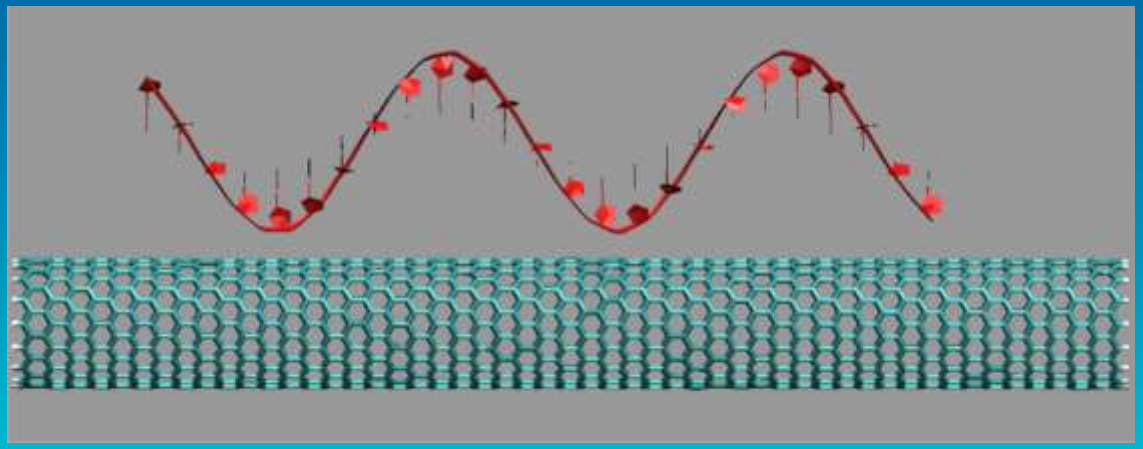
B-conformation
14026, 13298 water molecules
SWCNT zigzag (16,0)
Length-110 Å
Diameter-11.22 Å

First-Principles Calculations of the Interaction between Nucleic Acid Bases and Carbon Nanotubes

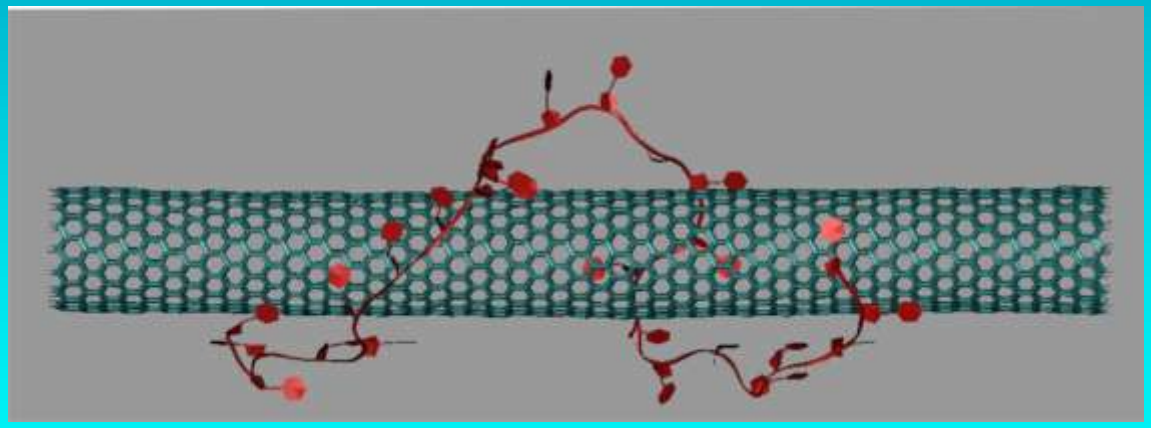
- Interaction energies between the between nucleic acid bases and single-walled carbon nanotubes were calculated at the MP2/6-31++G level of theory. The order is: Guanine (-16.0 kcal mol^{-1}) > Adenine (-14.1 kcal mol^{-1}) > Cytosine(-11.0 kcal mol^{-1}) ≈ Thymine(-10.9 kcal mol^{-1}) > Uracil (-10.5 kcal mol^{-1}).

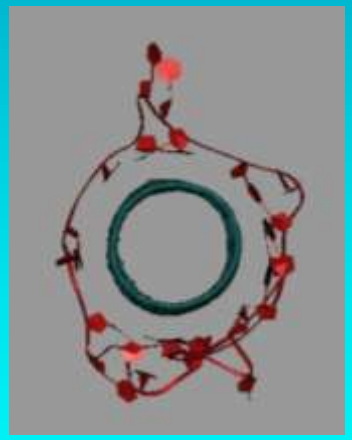
S.G. Stepanian, M.V. Karachevtsev, A.Yu. Glamazda, V.A. Karachevtsev, and L. Adamowicz. Raman Spectroscopy Study and First-Principles Calculations of the Interaction between Nucleic Acid Bases and Carbon Nanotubes. J. Phys. Chem. A, 113 (15), 3621-3629 (2009).

Molecular dynamic simulation of SWNT:polyC

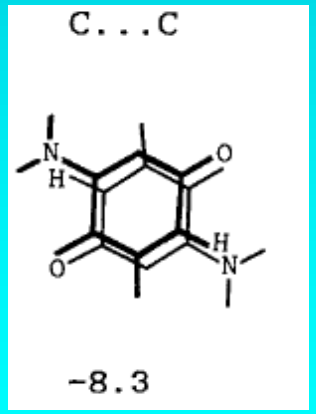


Molecular dynamic simulation demonstrates that some part of bases is out of stacking with the tube surface and some of them can form self-stacking structures. Competition between self-stacking and adsorption on the tube surface occurs.





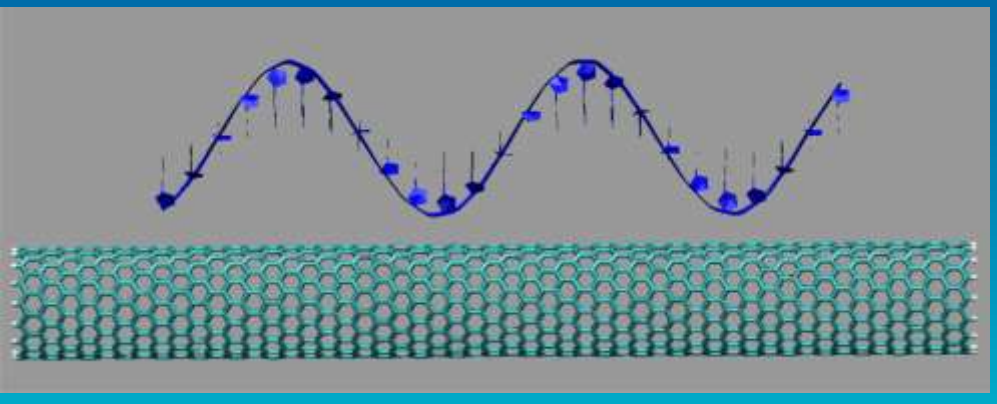
10 ns: 18 cytosines in stacking with tube (198); 2 dimers (C-C)
20 ns: 18 ; 30 ns: 20 cytosines (210) in stacking with tube; 2 dimers (C-C)

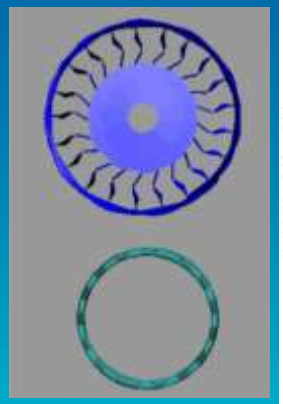


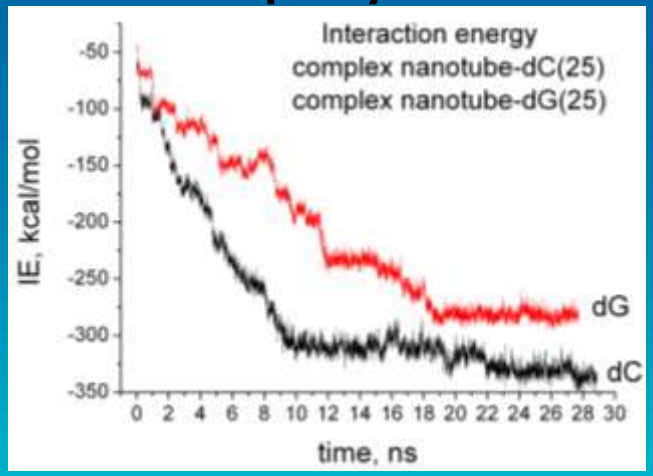
For simulation the program package NAMD was employed with Charmm27 force field parameter set. During simulation a box was applied, being of 50×60×135 Å dimensions in which poly(C)-wrapped SWNT was embedded in water (more than 11600 H_2O molecules). SWNT was selected as a zigzag (16.0) carbon nanotube. Its length and diameter were 11.0 nm and 1.27 nm, respectively. The 25-nucleotides length of poly(C) was selected. Step time simulation was 1 fs.

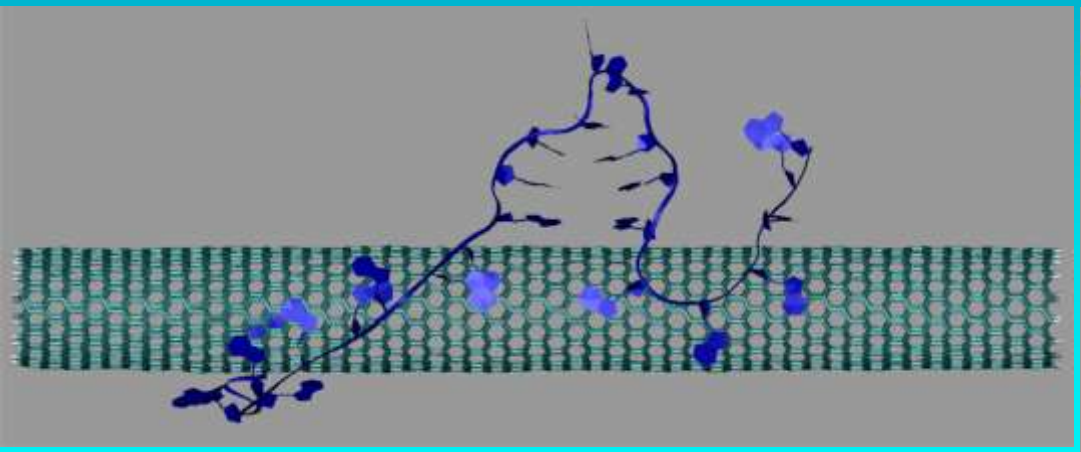
J. Sponer, J. Leszczynski, P. Hobza, Biopolymers 2002, 61, 3–31.

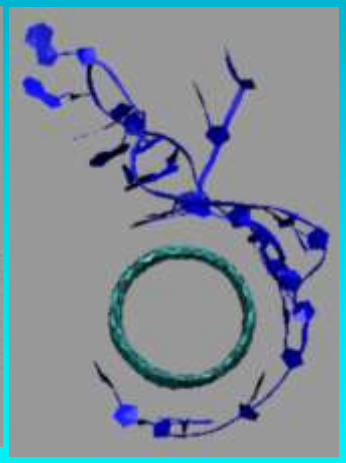
Molecular dynamic simulation of SWNT:polyG

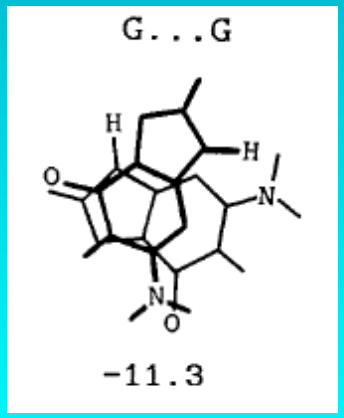












10 ns: 8 guanines in stacking with tube (128), 2 dimers (GG) and 3 quarters (GGGG)
20 ns: 14 guanines in stacking with tube (224), 2 dimers (GG) and 2 trimers (GGG)
30 ns: 14 guanines in stacking with tube (224), 2 dimers (GG) and 2 trimers (GGG)

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Conclusions

- Interactions of synthetic polynucleotides and ss- and ds-native DNA result in attenuation of the light absorption intensity of nanotubes in 300-400 nm range. Absorption attenuation revealed is conditioned by the hypochromic effect induced with the stacking interaction of nitrogen bases with the nanotube surface.

- The strongest changes are observed in the absorption spectrum of nanotubes covered with ss DNA while in the case with dsDNA this effect is significantly weaker. The hypochromic effect is manifested more markedly for the pyrimidine polynucleotide (poly(rC)) than for purine polymer (poly(rG)), because of a higher ability of pyrimidine bases for structural reorientation.