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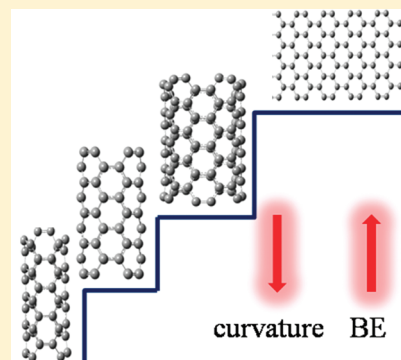
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S Supporting Information

ABSTRACT: Quantum chemical calculations reveal that the binding energy of the carbon nanotube (CNT) and DNA/RNA nucleobase complexes is controlled by the curvature of the carbon nanotube. Graphene not only has higher affinity but also appears to be best suited to differentiate various nucleobases compared with carbon nanotubes. The dispersion-corrected DFT and M06-2X functionals are in excellent agreement with the experimental observations. Interestingly, nucleus-independent chemical shift (NICS) calculations indicate substantial enhancement of aromaticity for all nucleobases upon binding to graphene and CNT.

SECTION: Nanoparticles and Nanostructures



Honeycomb network-based carbon nanostructures (CNSs) such as carbon nanotubes, graphene nanoflakes, and graphene have played a very important role in the pursuit of a plausible carbon-based nanotechnology, owing to their unique electronic, thermal, optical, mechanical, and transport properties.^{1–3} Graphene is a 2D system, and single-walled carbon nanotubes (SWNTs) are basically wrapped up graphene sheets in one dimension. Comparing the properties and reactivity of these two allotropes, which differ in their curvature, is interesting in its own right. The adsorption of various substrates such as gas molecules, metal ions, polymers, organic molecules, and biomolecules such as proteins and DNA on CNT surfaces has attracted considerable attention because of the fundamental importance and potential industrial applications.^{4,5} In particular, the DNA/CNT interaction has gained significant attention because of its application in various fields such as DNA sequencing, DNA sensing, and drug delivery.^{6–9} Recently, it has been found that the determination of a patient's DNA sequence can reveal the risk to fall ill with particular diseases and also helps to design “personalized medicine”, and thus the DNA sequencing appears to be one of the most potential applications for the carbon nanostructures.^{10–12}

Developing sensors based on CNT-biomolecule composites for amplified detection methods is an area of recent interest, and such sensors can be efficiently used to detect various different carbon nanostructures as well as different biomaterials such as DNA, protein, and so on.¹³ In addition, DNA-functionalized carbon nanotubes hold the exciting promise of forming the basis for new classes of chemical sensors and molecular electronic devices. An ultrasensitive graphene-embedded nanochannel device that effectively controls the motion of nucleobases via π - π

interaction was recently reported.¹⁴ Weizmann et al.¹⁵ recently reported that DNA–CNT nanowire networks can be used for DNA detection and Zheng et al.¹⁶ constructed a carbon nanotube-based DNA biosensor for monitoring phenolic pollutants. Apart from biomedical applications, understanding the CNT/DNA interaction can also be used in the separation of carbon nanotubes as it has been shown that single-stranded DNA can be effectively used for the dispersion and separation of single-walled carbon nanotubes.¹⁷ Several groups have focused on determining the DNA–CNT interaction and tried to explore the strength of binding of different nucleosides, nucleobases, and nucleobases pairs on the carbon nanotubes and graphene, in both experimental and computational studies.^{18–22} The experimental studies reveal different binding energy orders for different studies, and it is understood that this may be due to the different experimental conditions applied. In computational studies, for most cases, the order is $G > A > T > C > U$, and in some cases, they could not distinguish the nucleobases such as T, A, and C, and they have given the order as $G \sim A \sim T \sim C > U$. There are a number of theoretical experimental studies on the nucleobases interaction with carbon nanotube and graphene surfaces both experimentally and theoretically (Table 1).

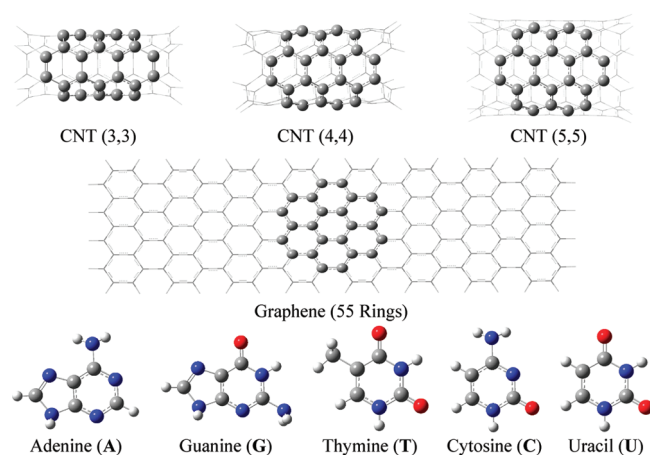
In this Letter, we attempt to investigate the effect of curvature in the honeycomb-based carbon nanostructures such as carbon nanotubes and graphene on the binding of the nucleobases. To cover a large range of curvature, we have considered graphene and single-walled arm chair carbon nanotubes models such as

Received: May 25, 2011

Accepted: June 8, 2011

Table 1. Collection of Binding Affinity Data for the Earlier Experimental (exp.) and Computational (comp.) Studies on Nucleobases Interaction with Carbon Nanotubes and Graphene

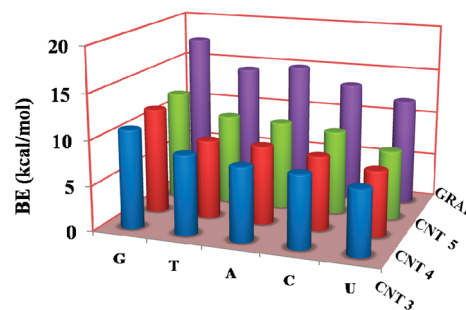
CNT				graphene		
type	order	method	ref	order	method	ref
SWNT	T A ~ C	exp.	17	G A C T	exp.	29
SWNT	G C A T	exp.	23	G A ~ T C	comp.	29
CNT (5,5)	T A C	exp.	24	G A ~ T ~ C U	comp.	30
CNT (5,5)	G A T C	comp.	24	G A T C U	comp.	31
CNT (5,0)	G A T C U	comp.	25			
CNT (10,0)	G A T ~ C U	comp.	26			
CNT (7,0)	G A ~ T ~ C U	comp.	27			
CNT (5,5), CNT (10,0)	G A T C	comp.	28			

Scheme 1

CNT (3,3), CNT(4,4), and CNT(5,5) as substrates (Scheme 1). The dangling bonds at the ends were saturated by hydrogen atoms. It is shown from the optimized structures that the nucleobases are oriented parallel above the surface of the CNS at a distance of around 3.2 to 3.3 Å. Figure 2 shows the top view of the orientation of the nucleobases on the carbon surface in the optimized geometry. As it can be easily noted from the Figure, the orientation of the nucleobases remains the same as the curvature of the carbon nanotube changes. Therefore, one can say that there is no appreciable change in the distance as well as the orientation of the complexes as the curvature varies.

The binding energy of all complexes considered in this study is graphically shown in Figure 1, which illustrates that the binding energy increases as the curvature decreases and reaches the maximum for graphene. In general, the nucleobases tend to have π - π stacking³² type of interaction with the carbon nanostructures. Hence, as the curvature decreases, there will be more efficient stacking between the carbon nanotube and the nucleobases surface, and we could easily expect an increase in the binding energy of the complexes. The effect of size and curvature generally plays an important role in the non-bonded interaction.^{33,34} Our results also reveal the same trend; that is, as we move from CNT (3,3) to graphene, the curvature decreases and the binding energy increases.

In general, the order of magnitude of physisorption energy is defined as lower than ~ 5 kcal/mol, whereas that of chemisorption

**Figure 1.** BSSE-corrected B3LYP-D/6-31G**/ONIOM(M06-2X/6-31G*:AM1) level BE of CNT and graphene with nucleobases.

energy is higher than ~ 12 kcal/mol. Recently, Chung et al.³⁵ reported a method to link reversibly DNA with SWNT, and such reversibility is important in the case of its application as sensors to detect DNA. Our calculations show that all three different CNTs possess binding energy within the range of ~ 7 to 12 kcal/mol, and thus they are within the range of physisorption and chemisorption. However, the binding energy of graphene with nucleobases is in the range of ~ 12 to 17 kcal/mol, which slightly exceeded the lower limit of chemisorption. Hence it appears from our study that for CNT complexes the adsorption and desorption are reversible at room temperature; however, it may be difficult in the case of graphene. We further investigated the HOMO–LUMO gap of the pristine CNS and their complexes. The energy difference between the HOMO and LUMO of the pristine CNS varies in the order CNT 3,3 (1.62) > CNT 4,4 (1.33) > CNT 5,5 (0.87) > Grap (0.07). This is in accordance with the observed binding energy values. However, there is no appreciable change in the HOMO–LUMO gap value upon complex formation in all complexes considered.

The computational studies at the B3LYP-D/6-31G**/ONIOM (M06-2X/6-31G*:AM1) level with BSSE correction show that the nucleobases bind to the carbon nanotube in the order $G > T \sim A > C > U$, and for graphene the order is $G > A > T > C > U$. The highest binding energy for the G complexes can be attributed to the fact that the orientation is such a way that there can be a possibility of NH- π interaction along with the π - π stacking interaction. It is also observed from Table 2 that the M06-2X result is in good agreement with the B3LYP-D (dispersion-correction) method.

We have also calculated the reorganization energy of the nucleobases and the charge transfer in the complexes and it

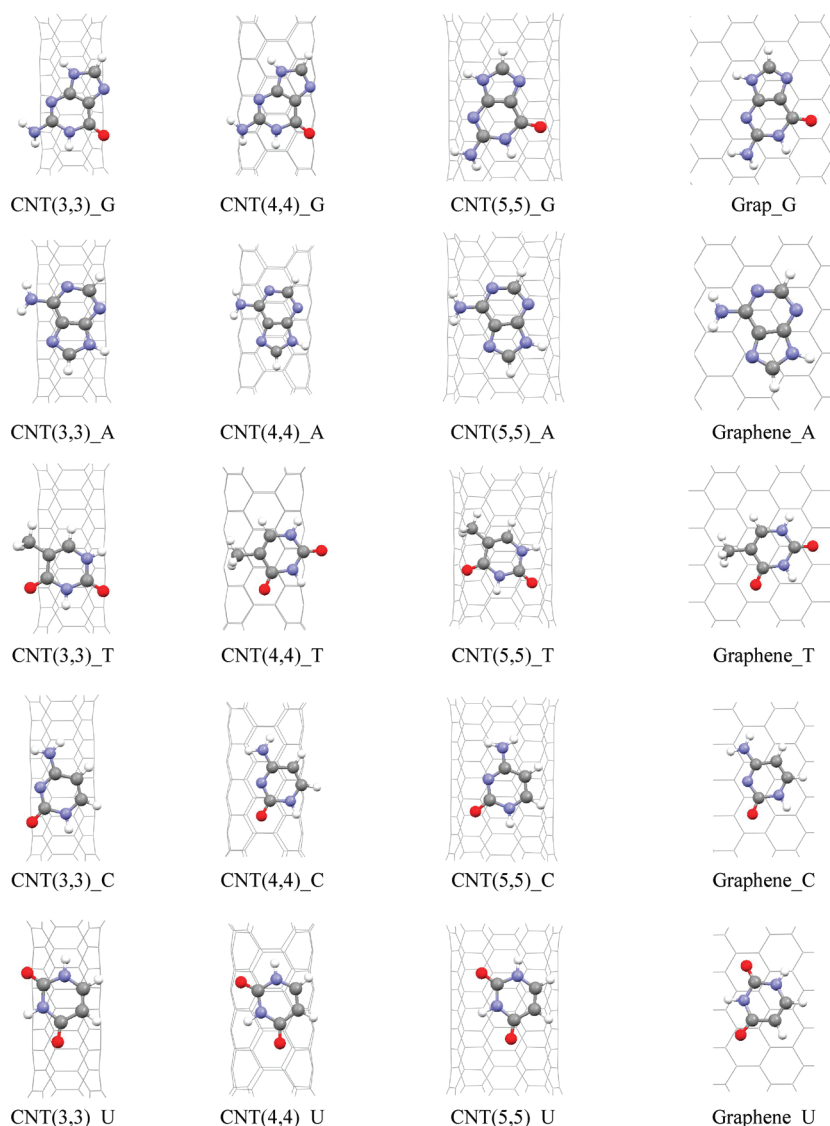


Figure 2. ONIOM (M06-2X/6-31G*:AM1) level optimized geometries of the nucleobases complexes with CNT of varying curvature and graphene (truncated view).

Table 2. Binding Energies (kilocalories per mole) of CNS-Nucleobase Complexs at Various Level of Theory^a

	CNT (3,3)			CNT (4,4)			CNT (5,5)			graphene		
	M1	M2	M3	M1	M2	M3	M1	M2	M3	M1	M2	M3
G	11.85	13.51	10.96	10.24	13.85	11.75	10.56	14.86	12.18	14.78	20.59	17.47
A	11.77	13.31	8.17	10.17	13.51	8.70	10.03	14.10	9.80	14.14	18.81	14.95
T	14.20	16.71	8.83	12.62	17.12	8.75	12.15	17.61	10.01	16.00	23.92	14.29
C	12.10	13.68	8.02	8.91	13.11	8.21	10.52	14.43	9.32	13.82	19.45	13.30
U	10.27	11.66	7.18	8.51	11.60	7.27	8.44	12.18	7.73	12.43	16.92	11.92

^a M1 = ONIOM (M06-2X/6-31G*:AM1); M2 = B3LYP-D/6-31G**/ONIOM (M06-2X/6-31G*:AM1); M3 = BSSE corrected B3LYP-D/6-31G**/ONIOM (M06-2X/6-31G*:AM1).

has been found that there is no appreciable deformation in the nucleobases structure. The natural bond orbital (NBO) analysis calculations were done with the aim of finding the charge transfer; however, the results declared that the charge transfer during the complex formation is negligible. (See the Supporting

Information.) The NICS values of the aromatic rings present in the nucleobases were calculated for the nucleobases in the pristine state and in the complex state. As it is known, the higher the negative value of the NICS parameter, the higher the aromaticity of the ring. It is clear from Table 3 that the

Table 3. NICS Parameter of the Various Aromatic Rings in the Parent Nucleobases and in the Complexes at M06-2X/6-31G* Level^a

	G		A		T	C	U
	Pyr	Imi	Pyr	Imi	Pyr	Pyr	Pyr
parent	-2.90	-12.80	-6.92	-12.43	-1.41	-1.11	-1.16
CNT(3,3)	-4.35	-14.02	-7.89	-13.43	-2.73	-2.31	-2.07
CNT(4,4)	-4.63	-14.50	-8.31	-13.88	-2.65	-2.65	-2.27
CNT(5,5)	-5.48	-15.12	-9.22	-14.79	-3.90	-3.22	-3.30
graphene	-7.28	-16.91	-10.93	-16.52	-5.66	-5.59	-5.66

^a Pyr = pyrimidine ring, Imi = imidazole ring.

aromaticity of the ring increases in the complex state and it is increasing as the curvature of the CNT increases. Hence, we can say that the binding energy of the nucleobases to the carbon materials increases the aromaticity of the nucleobase rings.

In sum, the present work provides the quantitative estimates of the binding energy values using highly reliable first-principle calculations for the five known nucleobases with the carbon nanostructures. The present Letter reports a clear inverse relationship between the curvature and binding affinity in carbon nanostructure, and the highest binding energy is observed for the least curved graphene and these results are in excellent agreement with the experimental observations. It is interesting to observe that the aromaticity of the nucleobases, as estimated by NICS criterion, increases significantly upon binding to both CNTs and graphene, with a dramatic extent in the later case. Thus, the current computational study proposes that graphene is endowed with better properties for DNA sequencing compared with CNTs. This observation should encourage a more focused research on graphene for possible applications for DNA sequencing.

COMPUTATIONAL DETAILS

The geometry of all complexes was optimized without any symmetry constraints using two-layer ONIOM calculations at the (M06-2X/6-31G*:AM1) level, in which the reaction center of carbon nanotubes and all atoms in the nucleobases were considered as the higher layer and the remaining as lower layer. This was followed by a single-point calculation using dispersion-correction method, B3LYP-D/6-31G*. Then, the interaction energy was corrected for basis set superposition error (BSSE). NICS calculations were carried out at M06-2X/6-31G* level of theory to characterize the aromatic nature rings of the nucleobases. The NBO charges of all systems considered were calculated at the M06-2X/cc-pVDZ level. All calculations were done in the Gaussian 09 suite of program.³⁶

ASSOCIATED CONTENT

Supporting Information. HOMO–LUMO energy gap of CNS–nucleobase complexes, geometries, NBO charges, reorganization energies, and NICS parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

CSIR, New Delhi is thanked for financial support and a senior research fellowship to D.U. We also thank DST is for Swarnajayanthi Fellowship to G.N.S.

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