# Noncovalent Interaction of Carbon Nanostructures

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CONSPECTUS: The potential application of carbon nanomaterials in biology and medicine increases the necessity to understand the nature of their interactions with living organisms and the environment. The primary forces of interaction at the nano—bio interface are mostly noncovalent in nature. Quantifying such interactions and identifying various factors that influence such interactions is a question of outstanding fundamental interest in academia and industry.

In this Account, we have summarized our recent studies in understanding the noncovalent interactions of carbon nanostructures (CNSs), which were obtained by employing first-principles calculations on various model systems representing carbon nanotubes (CNTs) and graphene. Bestowed with an extended sp^2 carbon network, which is a common feature in all of these nanostructures, they exhibit $\pi-\pi$ interactions with aromatic molecules (benzene, naphthalene, nucleobases, amino acids), cation—π type of interactions with metal ions, anion—π interactions with anions, and other XH···π type of interactions with various small molecules (H_2O, NH_3, CH_4, H_2, etc.). CNTs are wrapped-up forms of two-dimensional graphene, and hence, it is interesting to compare the binding abilities of these two allotropes that differ in their curvature. The chirality and curvature of CNSs appear to play a major role in determining the structural, energetic, and functional properties. Flat graphene shows stronger noncovalent interactions than the curved nanotubes toward various substrates.

Understanding the interactions of CNSs with organic molecules and biomolecules has gained a great deal of research interest because of their potential applications in various fields. Aromatic hydrocarbons show a strong propensity to interact with CNSs via the $\pi-\pi$ mode of interaction rather than CH···π interaction. As DNA sequencing appears to be one of the most important potential applications of carbon nanomaterials, the study of CNS—nucleobase interactions has become quite important. The nucleobases are physisorbed on the surface of CNSs in the order G > T ≈ A > C > U, exhibiting $\pi-\pi$-stacking type of interaction. These interactions become stronger as the curvature of the CNSs decreases. It is also indispensable to study the interaction of nanomaterials with proteins and especially with amino acids at a molecular level to understand the drug delivery mechanism of CNSs. We have shown that the CNSs interact with small molecules by means of physisorption and thus show potential for sensor applications. The prime requisite for the exploitation of these CNSs in nanoelectronics is the tunable energy gap. We have revealed that metal ion doping modulates the HOMO—LUMO energy gap of the nanotubes significantly and thus provides a handle to tune the electronic and conductivity properties of CNTs. Moreover, metal ions tend to selectively bind with nanotubes of different chirality such as armchair and zigzag nanotubes. The reduction of planar hydrocarbon materials by lithium atoms has also been studied very systematically. We also illustrate the way in which noncovalent interactions can be used to optimize and fine-tune the properties of CNSs.
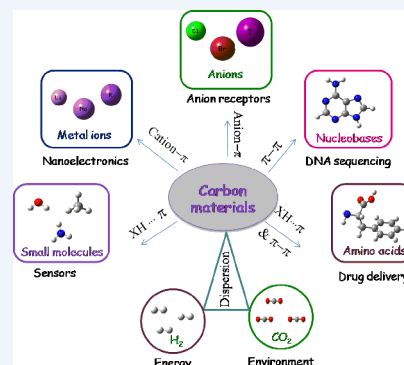
■ INTRODUCTION

Carbon occurs in several allotropic forms, and the physical and chemical properties of these allotropes vary widely. Diamond, graphite, and amorphous carbon such as charcoal, coke, and carbon black were the only known allotropes of carbon for a long time. A major breakthrough in carbon chemistry occurred in the recent past after the discovery of the newer allotropes such as fullerenes, carbon nanotubes (CNTs), and graphene.[1−3] Graphene, the youngest known allotrope of carbon, is a two-dimensional and one-atom-thick material consisting of sp^2-hybridized carbon atoms arranged in a honeycomb structure. Wrapping of graphene leads to CNTs; comparing the behaviors of these two allotropes (which differ in their curvature) toward various noncovalent interactions is interesting in its own right. As CNTs are hollow cylindrical tubes, molecules can not only be adsorbed on the surface but also be encapsulated inside the CNTs.[4] Several experimental and

theoretical studies have been done to compare the binding affinities of these two possible binding sites of CNTs. The different allotropes of carbon and the model systems used to mimic them are illustrated in Figure 1. The extended π-conjugation of these carbon nanostructures (CNSs) enables them to exhibit cation—π and $\pi-\pi$ type of noncovalent interactions with various substrates. The importance of cation—π interactions in chemistry, biology, and materials science is very well recognized,[5] and $\pi-\pi$ noncovalent interactions have also been extensively studied in recent years.[6] A systematic analysis of $\pi-\pi$ networks and their connectivity patterns present in proteins has been given in our recent database.[7] The relative strengths of CH···π and $\pi-\pi$
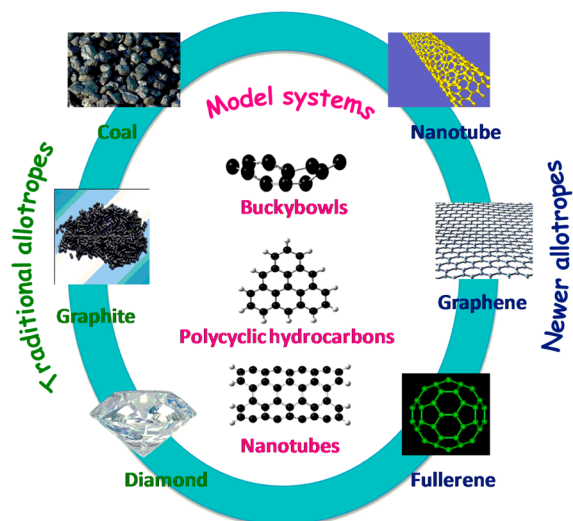
Figure 1. Schematic representation of various carbon allotropes and their model systems.

interactions in benzene clusters have also been addressed by our group.[8]

The physical, chemical, and electronic properties of CNTs largely depend on their curvature and chirality. Nanotubes can be classified into different types on the basis of their chiral indices, and their structures can be specified through their chiral vectors represented by the chiral indices (n,m). Armchair (n,n) nanotubes show metallic behavior, while zigzag $(n,0)$ nanotubes perform as semiconductors. Chiral (n,m) nanotubes exhibit metallic behavior if the difference between n and m is a multiple of 3; otherwise, they behave as semiconductors.[9] The formation of different CNSs from graphene is illustrated in Figure 2. Functionalization of CNTs by various species has been shown to provide a much easier manipulation of the nanotubes. Noncovalent functionalization of CNSs involves no bond making and bond breaking and hence appears to be the most efficient way to functionalize CNSs without disturbing the sp^2-hybridized π network.[10]
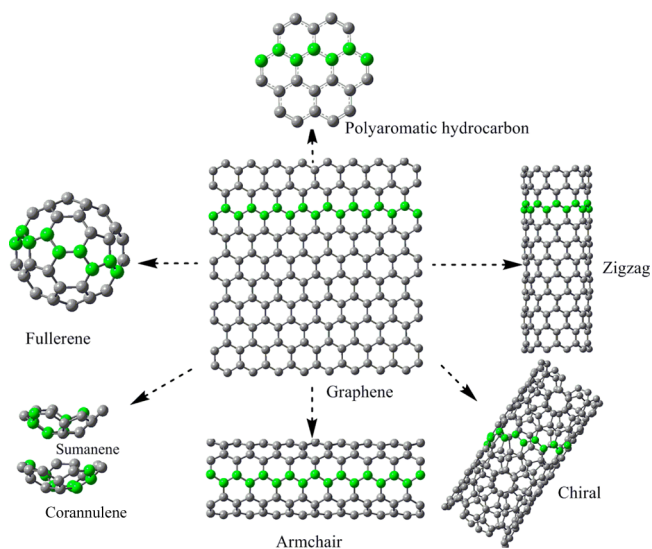

Figure 2. Schematic depiction of the formation of nanotubes, polyaromatic hydrocarbons, buckybowls, and fullerenes from graphene sheets.

NONCOVALENT INTERACTIONS

The unique physical, chemical, and electronic properties of CNSs make them appropriate for various potential applications in areas ranging from electronics to medicine. It has been shown in the literature that these CNSs exhibit noncovalent type of interactions with the substrates in many cases.[11] Hence, it has become important to quantify these noncovalent interactions and also to identify the factors that govern their strength. Besides, as nanomaterials show promising applications in biology and medicine, it is extremely essential to know how they interact with living organisms and the environment.[12]

Cation$-\pi$ interactions are arguably the strongest noncovalent interactions, and they have been extensively studied in recent years. The impact of solvation on cation$-\pi$ interactions involving various metal ions has also been reported in our earlier studies.[13−15] We have done extensive studies to show the effect of size and curvature of the π system on the binding energy of the cation$-\pi$ interaction.[16−20]

Though weak in nature, $\pi-\pi$ interactions are known to impart both structural and functional properties to materials as well as to biomolecules. CNSs have been shown to exhibit $\pi-\pi$ interactions with different aromatic groups in various biomolecules. The $\pi-\pi$ stacking interactions of CNSs with aromatic molecules appear to be of substantial significance because of their extended π conjugation, and they seem to play a significant role in explaining the versatile applications of CNTs and graphene.

Anion$-\pi$ interactions in the case of simple aromatic compounds are generally not very strong in nature. In recent research, however, anion$-\pi$ interactions between halide ions and graphene flakes have been found to be stronger than those with simple aromatic compounds like benzene. This unexpected strong binding has been attributed to the effective donor$-$acceptor interaction between the halide ions and the CNSs.[21]

The weak attraction between an X$-$H bond (X = C, O, N, etc.) and a π system is known as an XH$\cdots\pi$ interaction. These interactions have been considered to be a unique type of hydrogen-bonding interaction in which π electrons act as the proton acceptor.[22] Our group has done a series of studies of XH$\cdots\pi$ interactions involving various molecular cations and small molecules.[23−25]

INTERACTIONS WITH SMALL MOLECULES

The study of the interactions of small molecules with CNSs has been a topic of interest, as the electronic properties of the CNSs can be fine-tuned by the binding of small molecules. For instance, it has been reported by an experimental study that the conductance of CNTs is very sensitive to NH_3.[26] Dai and co-workers were the first to report the potential of CNTs to be used as gas sensors for the detection of molecules such as NO_2 and NH_3.[26] Schedin et al.[27] reported their experimental observation that graphene-based sensors could detect even the adsorption of individual gas molecules. In their experimental study, Meyyappan and co-workers reported small-molecule sensing of nanotubes in terms of a charge transfer mechanism.[28] Besides the interactions on the exterior surface, several studies have been done to understand the interactions of small molecules with the interior region of CNTs. Yim et al.[29] studied the interaction of CO_2 molecules with CNTs by employing both theoretical and experimental methods and reported that the adsorption energy is larger for
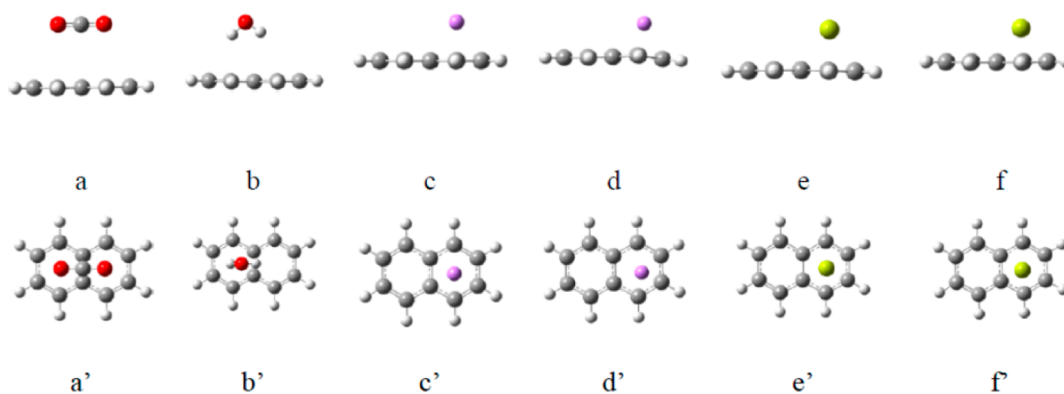
Figure 3. Modes of interaction of (a, a′) CO_2, (b, b′) H_2O, (c, c′) Li^+, (d, d′) Li, (e, e′) Mg^{2+}, and (f, f′) Mg with a graphene model. Reproduced from ref 31. Copyright 2011 American Chemical Society.

the interior region than for the exterior of the CNTs. It has also been shown in a recent study that the Gibbs energy of binding of CO_2 to the interior of the CNTs is higher compared with that to the exterior of the tubes.[30]

We employed first-principles calculations to study the interaction of small molecules such as CO_2, H_2O, metal atoms, and metal ions with graphene nanoflakes.[31] The orientation of the small molecules and metal ions on the graphene surface is illustrated in Figure 3. This study was later extended to CNTs and graphene nanoribbons for various small molecules and metal ions.[32,33] The interactions of metal ions with CNSs are elaborately discussed later in this Account, while the interactions of small molecules with CNSs are discussed here. We studied the interactions of various small molecules such as CO_2, H_2O, NH_3, CH_4, and H_2 with the surfaces of CNTs and graphene.[33] It has also been noted that these molecules act as charge donors to the CNSs. We showed the hierarchy of the binding of these gas molecules to be H_2O > CO_2 > NH_3 > CH_4 > H_2. We also observed significant changes in the polarizability of the CNSs upon binding with the gas molecules, and hence, we proposed that monitoring such changes may provide valuable guidance in designing gas sensors based on CNSs.[33]

INTERACTIONS WITH AROMATIC HYDROCARBONS

In the interactions between aromatic hydrocarbons there is a subtle competition between two comparable interactions, namely, CH⋯π and π−π interactions. Our computational studies on benzene clusters revealed that CH⋯π interactions are much more predominant compared with π−π interactions, which is also substantiated by the crystal structure of benzene.[8] Interestingly, a systematic analysis of the π−π networks in proteins revealed the existence of both CH⋯π and π−π interactions, with the former occurring most frequently.[7] In contrast to the above observations, when aromatic hydrocarbons interact with CNSs, π−π interactions clearly override the CH⋯π interactions.[34] In their ultrahigh vacuum kinetics experiments, Komarneni et al.[35] revealed the stronger interaction of benzene with the interior of CNTs compared with the exterior region. A systematic analysis has been done in order to study the mode of orientation of aromatic hydrocarbons such as benzene and naphthalene on the surface of CNSs. In general, aromatic hydrocarbons can have two possible orientations while interacting with conjugated π systems (Figure 4): the stacked orientation (S), in which the aromatic
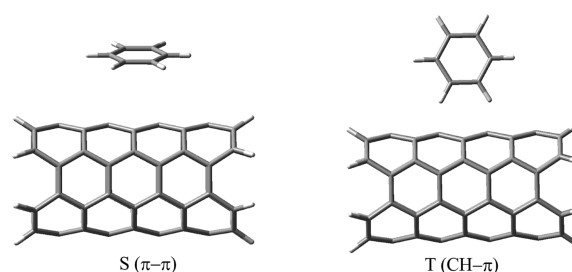

Figure 4. Different binding modes (S and T) of benzene with CNTs.

hydrocarbon is placed parallel to the plane of the π system, leading to π−π interactions, and the T-shaped orientation (T), in which the aromatic group is oriented perpendicular to the surface of the CNS, resulting in CH⋯π noncovalent interactions. It has been observed that aromatic hydrocarbons prefer to form stacked complexes with CNSs rather than the T-shaped complexes. Interestingly, the energy difference between the stacked and T-shaped orientations is greater for planar graphene than for curved CNTs. Graphene exhibits stronger interactions with aromatic hydrocarbons than CNTs do. We have also observed that zigzag CNTs preferentially bind with aromatic hydrocarbons compared with armchair CNTs. These observations gleaned from the study of aromatic hydrocarbons have been applied to understand the behavior of biomolecules such as amino acids and nucleobases toward CNSs.

INTERACTIONS WITH AMINO ACIDS

The interactions of CNSs with various biologically important molecules have emerged as a topic of great interest because of their potential applications in biology and materials science.[36] Subramanian and co-workers have brought added insights on the interaction of peptides with CNTs.[37−40] Understanding the interactions of amino acids with CNSs is of key importance in the study of CNS−protein interactions, as illustrated in Figure 5. Piao et al.[41] employed spectroscopy and thermal analysis methods to investigate the interaction of amino acids with CNTs and reported that the adsorption is more favored for smaller-diameter CNTs. The effect of CNT tube size on the spontaneous encapsulation of proteins has also been investigated.[42] The importance of the aromatic contents of the amino acids in CNT−protein interactions has been demonstrated in a recent experimental study.[43] Ge et al.[44] observed that the aromatic residues of proteins play a significant role in the interactions between CNSs and proteins. Motivated by
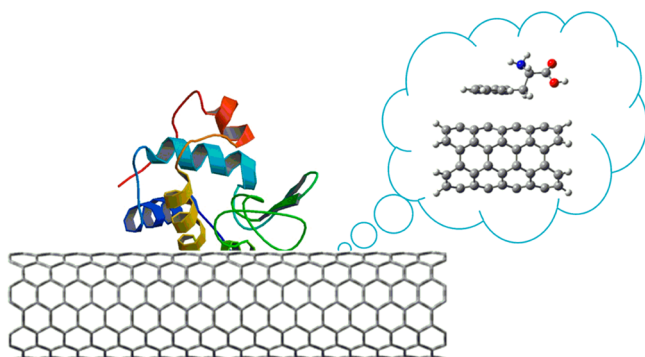
Figure 5. Schematic representation of the interaction between a CNT and a protein. The CNT and amino acid models used to mimic this interaction are shown in the inset.

these experimental results, several theoretical investigations on the interaction of aromatic amino acids with the CNSs have been reported.[45,46]

We have also performed a detailed analysis of the interactions of various aromatic amino acids such as Phe, Tyr, Trp, and His with CNSs.[34] Our study mainly focused on understanding the effect of the curvature and chirality of the CNSs on the interactions with aromatic amino acids. In order to explore the effect of the nanostructure's curvature, we considered both curved and the corresponding planar CNSs. Our study revealed that the binding affinity for aromatic molecules to a planar graphene surface is higher than that to a curved CNT surface. Among the CNTs considered, zigzag CNTs exhibit stronger binding affinities to the amino acids than armchair CNTs. The polarizabilities and HOMO energies of the CNSs were invoked to explain the observed selectivity. It was also noted that nucleus-independent chemical shift (NICS) values of the aromatic molecules increase upon binding with the CNSs and that the increase was observed to be more significant for graphene than for CNTs.[34]

INTERACTIONS WITH NUCLEOBASES

DNA sequencing is one of the very actively examined fields where CNSs show potential applications. In order to get a fundamental understanding of the CNS−DNA interactions, it is essential to study the interactions of nucleobases, the building blocks of DNA, with CNSs (Figure 6). Gowtham et al.[47,48] reported one of the earlier studies on the interactions of nucleobases with graphene and CNTs. Studies by Rao and co-
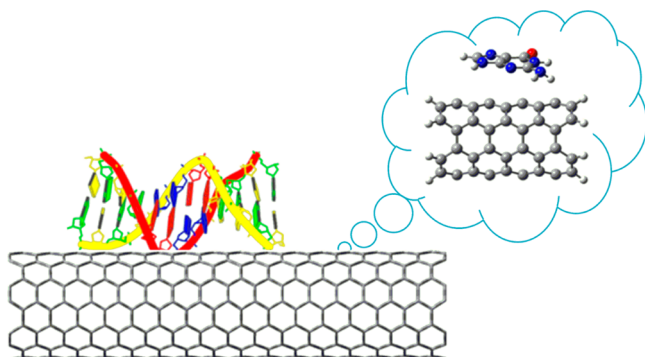

Figure 6. Schematic representation of the interaction between a CNT and DNA. Models used to mimic the CNT−nucleobase interaction are shown in the inset.

workers[49,50] and Grimme and co-workers[51] provided further insights into the relative binding affinity of nucleobases with CNSs. Through a detailed quantum-chemical analysis, Panigrahi et al.[52] showed the importance of $\pi-\pi$ stacking interactions in stabilizing the graphene−nucleobase complexes. CNSs have also been found to be good carriers of small interfering RNA (siRNA), and the binding mechanism of siRNA with CNTs and graphene has been studied extensively. It has been shown that the siRNA unzips on the surface of the graphene and wraps itself around the CNTs.[53,54] Cruz et al.[55] demonstrated that the encapsulation mechanism of nucleobases in CNTs is energetically favorable and reversible. In an experimental study, scanning tunneling microscopy was employed to reveal the structure of DNA−CNT complexes.[56]

We have done a systematic study of the interactions of various nucleobases with CNTs of different curvature and graphene using first-principles calculations.[57] CNTs with different diameters were considered to study the effect of curvature on the nucleobase binding. We have shown that the strength of the interaction of nucleobases with CNSs is controlled by the curvature of the CNSs.[57] Graphene shows a higher binding affinity than the curved CNTs and also was found to be best-suited to differentiate various nucleobases compared with nanotubes. This can be seen in Figure 7, where
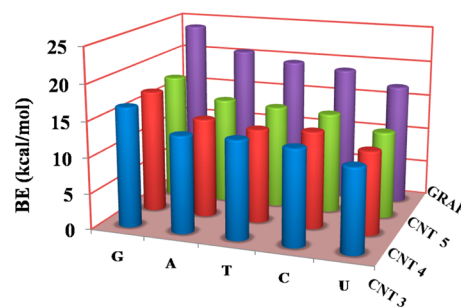

Figure 7. Binding energies of CNTs and graphene with nucleobases. Reproduced from ref 57. Copyright 2011 American Chemical Society.

the binding energies of different nucleobases with CNTs have been plotted. The order of binding energy of nucleobases has been obseved in our computational study as G > T ≈ A > C > U for CNTs and G > A > T > C > U for graphene, which is in good agreement with the experimental results.[57] The highest binding strength of the G complexes may be credited to the possibility of NH···π interactions in addition to the $\pi-\pi$ stacking interactions with the CNSs. We also noted that the aromaticity of the nucleobases, as estimated by the NICS criterion, increases significantly upon binding to both CNTs and graphene, with a dramatic extent in the latter case.[57]

REDUCTION OF CNSS BY LITHIUM

Binding of lithium to CNSs is a topic of industrial interest as lithium ion batteries are used in portable electronic devices as the energy source. The reversible capacity of the battery depends on the type of cathode and anode materials.[58] Graphite, one of the allotropes of carbon, is used as the principal candidate in lithium ion batteries. The unique tubular structure of CNTs makes them a promising candidate for confinement of elements and encapsulation of molecules.[59,60] Through a series of experiments and extensive studies, Bao and co-workers reported the role of the CNT channel in facilitating metal reduction[61] and catalytic reactivity.[62] The recent Account

by Pan and Bao also discussed the difference in the catalytic activities of metals and metal oxides at the interior and external surfaces of the CNT, which provides a lot of information.[63] A systematic attempt was carried out to understand sequential lithium adsorption on the carbonaceous materials, which is expected to provide the utilities of these materials in various areas.[64] Small polyaromatic hydrocarbons (PAHs) such as benzene, naphthalene, anthracene, and tetracene were considered as prototypical carbonaceous materials that can mimic CNSs. Lithium adsorption on these materials at all possible adsorption sites was studied using density functional theory (DFT). The study found that sequential adsorption of lithium atoms on the carbonaceous materials is very feasible in nature. The most stable complexes were observed when lithium gets adsorbed to both sides of the plane of the PAH molecules. Charge transfer analysis also showed the ability of lithium to reduce carbonaceous materials. We also noted that the binding of the first lithium dramatically facilitates the binding of the second lithium in most cases.[64] This study provides very strong evidence of the reduction capability of lithium atoms, and we expect to get similar trends when larger hydrocarbons such as graphene and CNTs are considered as the model systems.

INTERACTIONS WITH METAL IONS

Metal ions interact with the extended π conjugation of the CNSs and exhibit cation−π interactions. It has been shown that CNTs can be effectively employed as sorbents to remove metal ion pollutants from wastewater.[65] We studied the interactions of metal ions such as Li^+ and Mg^{2+} with graphene nanoflakes. Various linear (Ln) and branched (Bn) polycyclic aromatic hydrocarbons were used to model the graphene surface, as shown in Figure 8. In the case of Ln, as we move from L1 to
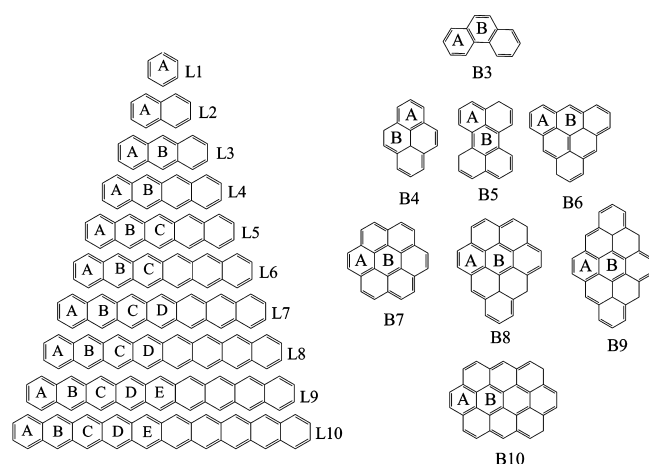

Figure 8. Linear (Ln) and branched (Bn) polycyclic aromatic hydrocarbons. Reproduced from ref 31. Copyright 2011 American Chemical Society.

L10, metal ion binding increases with the increase in the number of rings, and the highest binding energy value is obtained for the largest PAH, L10. However, in the case of Bn, there is no such linear dependence of the binding energy on the size of the system. The polarizabilities and HOMO energies of the PAHs were used to uncover the origin of this difference.[31] Figure 9 illustrates the correlation between the polarizability of the graphene nanoflakes and the interaction energy.

Later, we extended this study to various alkali (Li^+, Na^+, K^+) and alkaline-earth (Be^{2+}, Mg^{2+}, Ca^{2+}) metal ions with CNTs

and graphene. In the optimized geometry, the metal ion orients itself above the center of a six-membered ring at a distance of around 1.8 to 2.0 Å. We also enumerated the effect of the curvature and chirality of the CNSs on their interactions with metal ions. The effect of curvature on the cation−π interactions with CNSs such as sumanene and corannulene was explored in our earlier studies.[16,17,20] We showed that graphene exhibits marginally stronger binding with the cations than the curved CNTs. The preference for binding of alkali and alkaline-earth metal ions are quite opposite toward CNTs with different chirality: alkali metal ions (Li^+, Na^+, K^+) prefer to bind with armchair CNTs, and the alkaline-earth metal ions (Be^{2+}, Mg^{2+}, Ca^{2+}) selectively bind with zigzag CNTs. A plausible explanation for this difference was given by invoking HOMO energy stabilization of the CNTs by the metal ions.[32]

Thus, we proposed that such preferential binding with CNTs would be of useful guidance in separating armchair and zigzag CNTs, which is one of the most important issues to be resolved for their practical applications in various fields. We note that Kim and co-workers subsequently showed the possibility of noncovalent functionalization with alkali metal to separate semiconducting from metallic CNTs.[66] Tuning the energy gap of nanomaterials is one of the important aspects in designing materials with desired electrical properties. Previously Lee et al.[67] demonstrated a conductivity enhancement in K- and Br-doped CNT bundles. We observed significant changes in the HOMO−LUMO energy gap of the CNTs upon metal ion binding, and thus, we proposed that fine-tuning of the energy gap of CNTs may be achieved through metal ion binding.[32]

GENERAL TRENDS, DIFFERENCES, AND SIMILARITIES IN THE NONCOVALENT INTERACTIONS OF CNSS

In this section, we qualitatively compare the binding strengths of CNSs toward different species and also shed light on the binding abilities of different CNSs. It has been shown from our earlier observations that small molecules such as CO_2 and H_2O interact with CNSs by physisorption with lower binding energies, whereas metal atoms and ions interact by chemisorption with higher binding energies.[31] Aromatic molecules interact with CNSs via $\pi-\pi$-stacking interactions with moderate binding energies that are in between those for metal ions and small molecules.[34] In general, it has been shown in many cases that the binding energy increases as the size of the system interacting with the CNS increases. The binding affinity also depends on the type of CNS, as graphene shows stronger binding affinity than curved CNTs in most cases.[32,34] For aromatic hydrocarbons and biomolecules, zigzag CNTs bind more strongly than armchair CNTs. However, in the case of alkali metal ions, armchair CNTs show stronger binding than zigzag CNTs (Figure 10). Thus, noncovalent functionalization of CNSs could be used as a tool to separate armchair and zigzag CNTs.

SUMMARY

The emergence of CNSs as promising materials in biology and medicine for use in drug delivery systems, DNA sequencing, and diagnostic tools warrants quantitative understanding of the nature and strength of the fundamental forces acting at the nano−bio interface. CNSs, bestowed with sp^2-hybridized carbon networks, are π systems that are optimally disposed to engage in cation−π, anion−π, $\pi-\pi$, and XH···π type of

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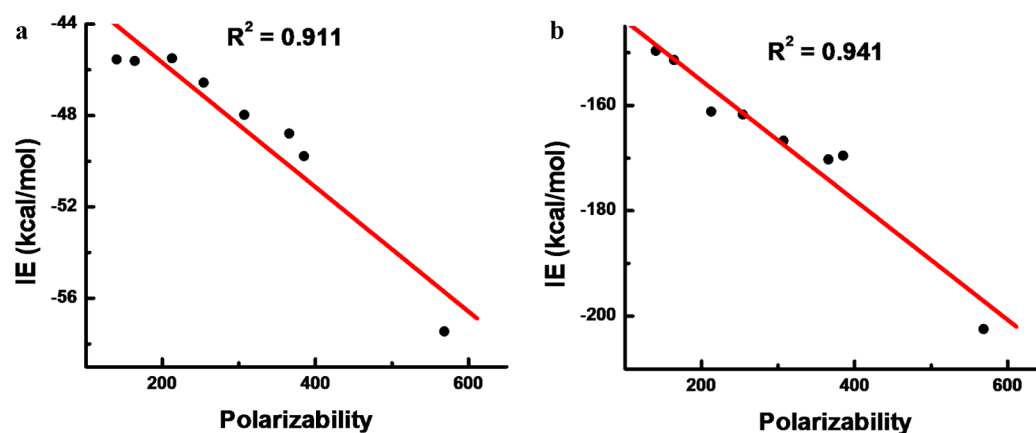dx.doi.org/10.1021/ar500168b | *Acc. Chem. Res.* 2014, 47, 2574−2581

Figure 9. Correlation between the polarizability (in au) of linear PAHs (Ln) and the interaction energy (IE) of their complexes with (a) Li$^+$ and (b) Be^{2+} metal ions. Reproduced from ref 31. Copyright 2011 American Chemical Society.
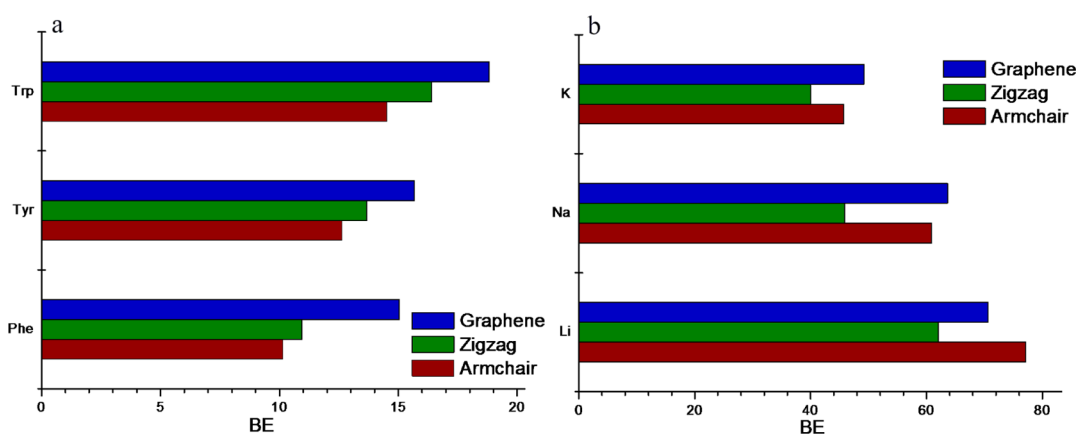

Figure 10. Binding energies (BE in kcal/mol) of different CNSs with (a) aromatic amino acids (data from ref 34) and (b) metal ions (data from ref 32).

interactions with small and large molecules. Accurate quantum-mechanical calculations have been employed to examine the interactions of various CNSs such as CNTs, graphene, and their siblings such as buckybowls and PAHs with varying curvature and chirality, and the results have revealed that these structures are optimally suited to engage in a range of noncovalent interactions, albeit with varying strengths. Alkali and alkaline-earth metal ions have been found to bind strongly and selectively to CNSs and to modulate the conducting nature of these materials dramatically. Our studies have revealed a systematic dependence of the binding of small molecules on the curvature and chirality in addition to the nature of the binding molecules. These accurate quantum-chemical calculation results can be effective when coupled with more approximate quantum-mechanical methods and classical molecular dynamics simulations to develop multiscale approaches that can conquer the modeling of larger assemblies. Interestingly, chemical reduction through lithium, which is of pragmatic industrial importance, displays dramatic trends. In most cases, the binding of the first lithium dramatically facilitates the binding of the second lithium. Also, these CNS materials seem to have very high uptake ability of lithium metal, making them promising materials. Thus, understanding noncovalent binding to CNSs through first-principles calculations will help to optimize and fine-tune the desirable properties in CNSs and also provide valuable guidance in designing advanced carbon materials for various desired applications. Thus, quantum-mechanical

calculations are indispensable in obtaining comprehensive and accurate descriptions of the interactions and properties of CNSs.

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G. Narahari Sastry obtained his early education in Andhra Pradesh, Bachelor's and Master's degrees from Osmania University, and a Ph.D from the University of Hyderabad under the supervision of Professor E. D. Jemmis. After a couple of postdoctoral stints with Professor Sason Shaik and Professor Thomas Bally, he started his independent career in 1997 at Pondicherry University. In 2002, he moved to the CSIR Indian Institute of Chemical Technology, Hyderabad, to head the Centre for Molecular Modeling Group. He has wide-ranging research interests in computational chemistry, biology, and materials science. The focus of the group currently is on understanding the way in which noncovalent interactions operate in chemical, biological, and nanomaterials systems. He has published over 230 scientific papers and in 2011 was awarded the Shanti Swarup Bhatnagar Award, the highest prize for science in India, in Chemical Sciences.

■ ACKNOWLEDGMENTS

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