

Cation- π interaction of alkali metal ions with C₂₄ fullerene: a DFT study

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Abstract Using first principle calculations, we investigated cation- π interactions between alkali cations (Li⁺, Na⁺, and K⁺) and pristine C₂₄ or doped fullerenes of BC₂₃, and NC₂₃. The most suitable adsorption site is found to be atop the center of a six-membered ring of the exterior surface of C₂₄ molecule. Interaction energies of these cations decreased in the order: Li⁺>Na⁺>K⁺, with values of -31.82, -22.36, and -15.68 kcal mol⁻¹, respectively. It was shown that the interaction energies are increased and decreased by impurity doping of B and N atoms in adjacent wall of adsorption site, depending on electron donating or receptivity of the doping atoms.

Keywords *Ab initio* · Adsorption · Doping · M05 · Nanostructure

Introduction

Discovery of buckminsterfullerene C₆₀ [1], and carbon nanotubes (CNTs) [2] has initiated a new era in supramolecular and

nanostructure chemistry [3–12]. The unique structural and electronic properties of fullerenes and CNTs are related to their particular geometrical arrangement of carbon atoms, widely studied both experimentally and theoretically [13, 14]. Compared to other carbon structures, fullerenes have revealed promising applications in a wide variety of very important technological processes such as designing electronic devices, superfibers, catalytic materials, etc.

Recently, much more attention has been focused on small carbon clusters [15, 16]. The interest in the small fullerenes is not only due to their relevance in gaining further understanding of C₆₀, but also the possibility of being an intermediate in the formation of C₆₀ and large fullerenes. Several theoretical studies have been devoted to the structure and stability of C₂₄ isomers [17–19]. Density functional theory (DFT) calculations have been performed by Jones [20] for many isomers of neutral carbon clusters C_n (4 ≤ n ≤ 32) using both local spin density (LSD), and gradient-corrected (Becke-Perdew) approximations to the exchange-correlation energy. Based on his findings, stable isomers include chains, rings, cages, and graphitic (“plate” and “bowl”) structures. He observed a fourfold periodicity in several structural classes as n changes. He also found that, stable cages exist for all clusters with n ≥ 8, and double rings are less stable than the monocyclic rings in all cases. The ground-state structure of D₆-symmetrical C₂₄ has also been observed [21].

Interaction of alkali metals with carbonaceous surfaces has been studied for years due to the interest in basic mechanisms of adsorption as well as for practical reasons [22]. The alkali metal ions with simple electronic structure are promising candidates for investigation of cation- π interaction with aromatic rings of fullerene. The interaction of Cation- π , also known as the Dougherty effect, is a non-covalent molecular interaction between the face of an electron-rich π system (e.g., benzene, fullerene) with an

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adjacent cation (e.g., Li^+ , Na^+) [23, 24]. Cation– π interaction energies are of the same order of magnitude as hydrogen bonds or salt bridges, and play an important role in molecular recognition. The electronic properties of the substituent also have influence on the strength of the attraction and the ring fusion to benzene has been the subject of recent theoretical interest [25–29].

In this investigation, calculations based on DFT were performed to address the interaction of cations of Li^+ , Na^+ and K^+ with a pristine C_{24} or doped fullerenes of BC_{23} and NC_{23} . These doped fullerenes have been frequently investigated to date [30, 31]. Also, the doping effects of B and N were theoretically investigated on atomic Li adsorption on fullerene molecule [32]. This kind of computational investigations would be helpful in designing novel molecular receptors for ion recognition. Molecular recognition has attracted great attention not only in chemistry, but also in biology [23]. Design and synthesis of new recognizer materials are important in removing radioactive and metal ions from waste water streams.

Computational methods

Geometric optimizations and all energy calculations were performed on a C_{24} fullerene and different alkali cation/fullerene complexes at the spin-unrestricted M05/6-31G* level of theory. Truhlar *et al.* recommended M05 functional for general purpose applications in noncovalent interactions involving both metallic and nonmetallic elements, among several studied functionals [33]. Studying the performance of 22 DFT methods in energetic calculations, Handzlik has shown that the M05 is one of the most accurate functionals in prediction of the energies of the proposed test reactions [34]. Kona and Tvaroska have shown that the results of M05 in prediction of structures and energies are closer to those of the computationally expensive MP2 method in comparison with those of that obtained using the well-known B3LYP one [35]. Moreover, even when tested on a wide variety of species, M05 had 55% lower mean unsigned error (MUE) than the B3LYP functional [36]. Several reports on the accuracy of this functional are available in the literature [37–40].

Subsequently, we investigated the influence of impurity doping on the cation– π interaction, substituting one carbon atom of C_{24} by B or N atom. Frequency calculations were performed at the same level, confirming that all of the structures are minima on their respective potential energy surfaces. The interaction energy (E_{in}) of alkali cations is defined as follows:

$$E_{\text{in}} = E(\text{cation/cluster}) - E(\text{cluster}) - E(\text{cation}), \quad (1)$$

where $E(\text{cation/cluster})$ is total energy of the alkali cation adsorbed on the pristine or doped C_{24} , and $E(\text{cluster})$ and $E(\text{cation})$ are the total energies of the pristine or doped C_{24} and the cation, respectively. By the definition, a negative value of E_{in} corresponds to a stable process. All calculations reported here were carried out using a locally modified version of the GAMESS electronic structure program [41].

Results and discussion

Optimized structure of C_{24} fullerene has D_6 symmetry and there are different C–C bonds with calculated lengths of 1.41–1.51 Å (see Fig. 1). Calculated DOS of the pristine C_{24} has been shown in Fig. 1, indicating that the C_{24} has a HOMO-LUMO gap (E_g) of 2.20 eV, suggesting that it is a semiconducting substance. Computed carbon-13 nucleic magnetic resonance (^{13}C -NMR) shows that the C atoms located at the hexagonal rings have the smallest chemical shielding isotropic values. The vibrational frequencies of the pristine C_{24} are found to be in the range of 104.6–1552.2 cm^{-1} . The smallest frequency (104.6 cm^{-1}) belongs to a twisting mode of the cluster and the largest frequency (1552.2 cm^{-1}) to the stretching mode of C–C bonds which is shared among four pentagonal ring, showing its more double character in comparison to the other.

We considered the interaction of Li^+ , Na^+ , and K^+ with the exterior surface of pristine C_{24} . To this aim, the ions were initially placed on various sites of fullerene surface (e.g., on-top of a carbon site, atop the center of hexagonal and pentagonal rings, or groove of a C–C bond). To ensure that the most stable adsorption configuration was achieved, the initial distance between the molecule and the cluster was adjusted several times from 1.0 to 3.0 Å. Full structural relax optimization was then performed with each initial ion-fullerene distance. Consequently, we found that the most favorable adsorption site is atop the center of hexagonal ring. As the main purpose of the present work was cation– π interactions, we focused on the cation adsorption atop the hexagonal and pentagonal rings.

Stable adsorption configurations of the ions on the hexagonal ring of C_{24} are shown in Fig. 2a. The calculated E_{in} values for adsorptions of Li^+ , Na^+ , and K^+ are -31.82 , -22.36 , and -15.68 kcal mol^{-1} , respectively (Table 1). These data indicate that the order of stability of the complexes is: $\text{C}_{24}\text{-Li}^+ > \text{C}_{24}\text{-Na}^+ > \text{C}_{24}\text{-K}^+$. These findings can be clearly defined by the fact that electrostatic interactions play a significant role in cation– π interaction of alkali ions and C_{24} , which is in good agreement with Deb's study [42]. The Li^+ ion has higher positive charge density due to its small size, thus electron affinity of Li^+ is greater than that of the Na^+ and K^+ . Furthermore, the shortest distances between the three adsorbed cations and fullerene surface are 1.87, 2.37,

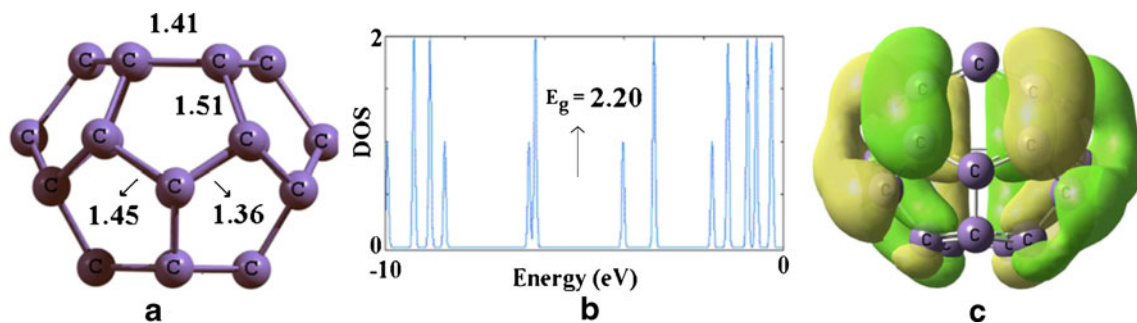


Fig. 1 (a) Geometrical parameters, (b) DOS plot, and (c) HOMO of optimized C₂₄. Distances are in Å

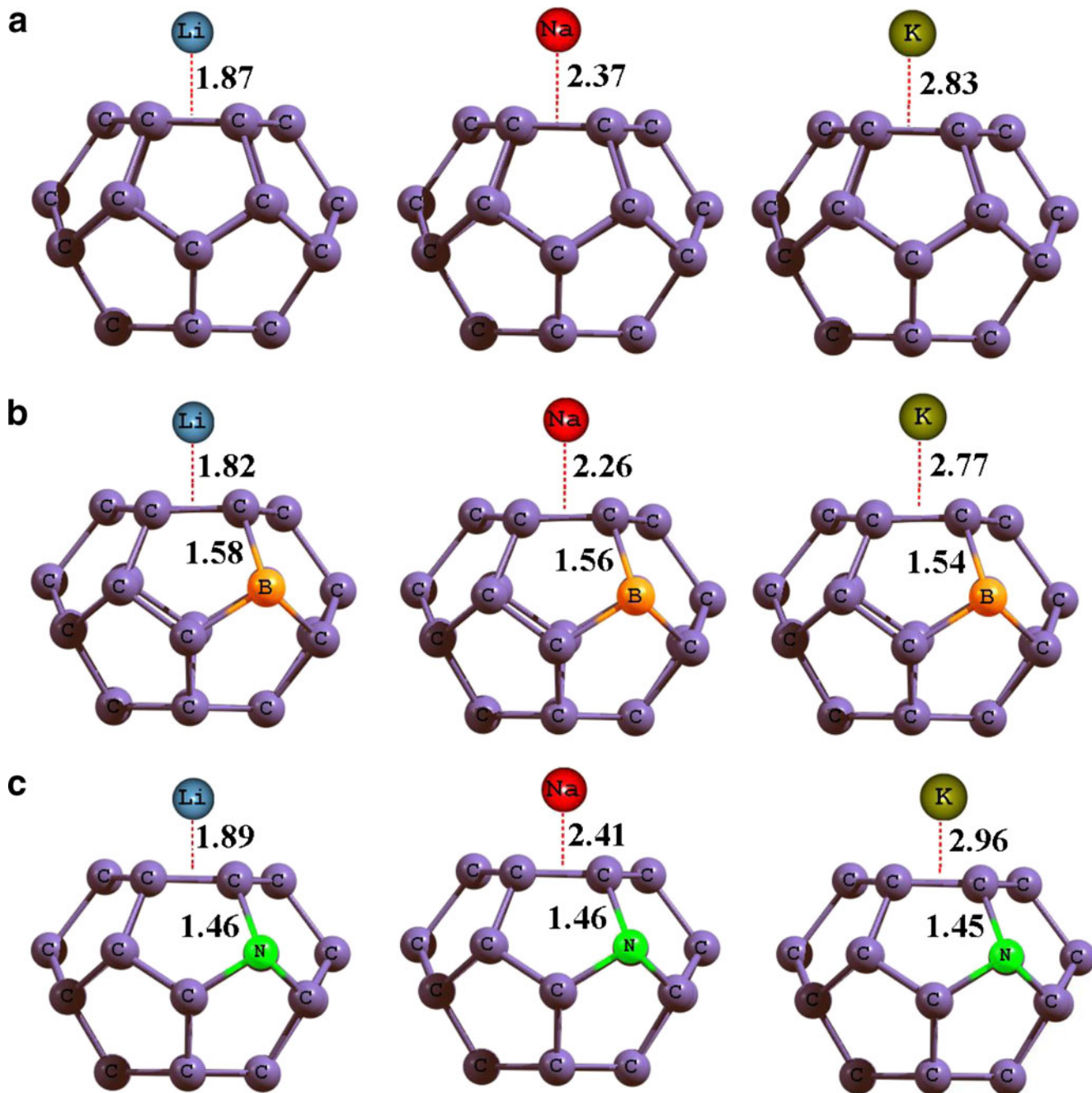


Fig. 2 Optimized structures of complexes of alkali cations with (a) C₂₄, (b) BC₂₃ and (c) NC₂₃. Distances are in Å

Table 1 Calculated interaction energies (E_{in}) and change of HOMO–LUMO energy gap (ΔE_g) for cation- π interaction of alkali ions with hexagonal ring of C_{24} fullerene

π -system	Cation	E_{in} (kcal mol ⁻¹)	^a ΔE_g (eV)
C_{24}	Li	-31.82	0.33
	Na	-22.36	0.29
	K	-15.68	0.25
BC_{23}	Li	-40.58	0.65
	Na	-31.36	0.59
	K	-24.44	0.55
NC_{23}	Li	-27.21	0.24
	Na	-18.67	0.20
	K	-11.30	0.17

^a The E_g of C_{24} , BC_{23} , NC_{23} are 2.13, 2.04 and 2.01 eV, respectively

and 2.83 Å. These distances are decreased in the order of $Li^+ < Na^+ < K^+$. The high E_{in} values indicate that the ions are strongly adsorbed onto the surface of pristine fullerene.

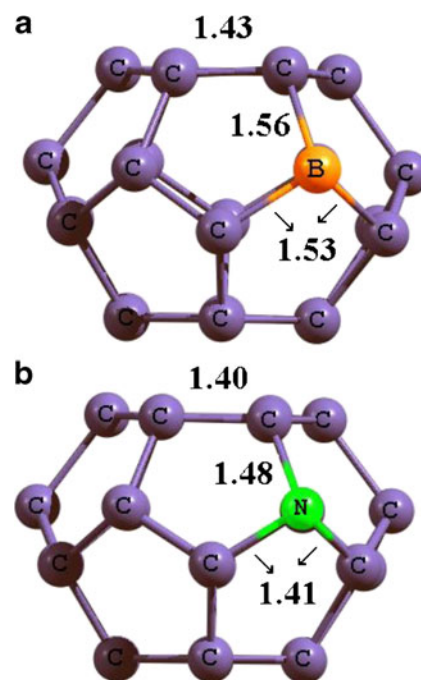
In the interaction between the cluster and ions, the cluster acts as an electron donor whereas HOMOs are composed of π orbital of the C_{24} rings (Fig. 1c), and the ions are electron acceptors so that the LUMOs contain them. We found that the presence of the alkali cations slightly increases the E_g of the pristine fullerene from 2.20 eV to 2.45–2.53 eV (Table 1). The calculated frequencies for cation/ C_{24} complexes are summarized in Table 2. As is shown in the table, ν_{max} of C_{24} is not significantly changed upon the adsorption process. As this frequency belongs to the stretching modes of C–C bonds, shared among four pentagonal rings far away from interaction area, therefore, it is expected that the cation adsorption cannot affect their length and strength. The frequencies of cations moving toward the center of hexagonal ring (ν_{cation}) are 296.2, 190.5 and 142.5 cm⁻¹, respectively for Li^+ , Na^+ and K^+ . It can be found that the ν_{cation} values are decreased by increasing the atomic mass of cations.

Table 2 Vibrational frequencies (cm⁻¹) of the studied systems.

ν_{min} and ν_{max} stand for minimum and maximum frequency of the systems, respectively

System	ν_{min}	ν_{max}	* ν_{cation}
C_{24}	104.6	1552.2	–
Li^+/C_{24}	102.4	1545.1	296.2
Na^+/C_{24}	87.4	1541.4	170.5
K^+/C_{24}	67.3	1540.2	142.5
BC_{23}	34.2	1467.6	–
Li^+/BC_{23}	88.1	1451.2	300.1
Na^+/BC_{23}	73.7	1462.5	174.3
K^+/BC_{23}	40.9	1476.3	134.7
NC_{23}	68.1	1519.1	–
Li^+/NC_{23}	87.0	1728.9	292.3
Na^+/NC_{23}	63.2	1741.6	163.3
K^+/NC_{23}	58.5	1759.3	154.2

* The frequencies of the cations moving toward the center of hexagonal ring

**Fig. 3** Optimized structures of (a) BC_{23} , (b) NC_{23} clusters. Distances are in Å

However, it is well known that the frequency and atomic mass are inversely related.

For group IV semiconductors, the most common dopants are acceptors from group III or donors from group V elements. Boron is a p-type dopant of choice for carbon integrated materials. Doping with B, which is missing the fourth valence electron, creates holes in the C_{24} lattice that are free to move. The result is an electrically conductive p-type semiconductor. In this context, N element is said to behave as an electron donor, and B element as an acceptor. By doping pure C_{24} with N, an extra valence electron is added that becomes unbonded from individual atoms and allows the compound to be an electrically conductive n-type semiconductor.

Table 3 Calculated interaction energies (E_{in}) and change of HOMO–LUMO energy gap (ΔE_g) for cation- π interaction of alkali ions with pentagonal ring of C_{24} fullerene

π -system	Cation	E_{in} (kcal mol ⁻¹)	ΔE_g (eV)	^a $D_{cation-cluster}$ (Å)
C_{24}	Na	-20.52	0.08	2.50
	K	-12.45	0.11	2.87
BC_{23}	Na	-25.82	0.12	2.43
		-17.29		2.82
NC_{23}	K		0.14	
				2.67
	Na	-17.52	0.26	3.08
	K	-8.99	0.24	

^a Equilibrium distance between cation and center of pentagonal ring of cluster

In the following, we investigate the effect of B and N doping into C_{24} on cation- π interaction between the target ions and the fullerene. As shown in Fig. 3, a carbon atom is substituted by a boron atom in C_{24} . For fullerene BC_{23} drastic changes in the geometrical structure of the C_{24} surface have been observed: the mean of three B-C bond lengths is 1.54 Å, which is quite large compared to 1.44 Å mean of the three C-C sp^2 bonds in pristine C_{24} .

After full optimization, E_{in} values for cation- π interaction of Li^+ , Na^+ and K^+ have been calculated. Compared to the pristine C_{24} , boron-doping enhances the E_{in} value of Li^+ , Na^+ and K^+ ions adsorbed on the similar site to -40.58, -31.36 and -24.44 kcal mol⁻¹ (Fig. 2b). Based on the Mulliken analysis, in BC_{23} , net charge on the B atom is 0.356 e. Electron donor substituent can increase charge density in aromatic ring of BC_{23} which will ease the π electron transfer to the target cation. Thereby, it is expected that the E_{in} of cations on BC_{23} be higher than that on the pristine C_{24} . Similarly Dougherty *et al.* [23] demonstrated that electron withdrawing groups (for example, -CN) weaken the cation- π interaction in benzene systems, while electron donating groups (for example, -NH₂) strengthen the cation- π binding. The origin of this effect is often attributed to the donation into or out of the π system. In the BC_{23} , the HOMO level is adjusted to -0.22 eV, and the E_g is 2.04 eV which is somewhat smaller than that of the pristine C_{24} . The ΔE_g values are 0.65, 0.59 and 0.55 eV for Li^+ , Na^+ and K^+ interaction with BC_{23} , respectively.

For the adsorption of alkali ions on the surface of NC_{23} , the adsorption site is similar to the former case, but here the dopant (B atom) is replaced by a nitrogen atom as shown in Fig. 3b. It should be noted that the fullerene lattice near the impurity atom is severely distorted, where the impurity N projects out of the C_{24} wall due to its larger size than the C atom and prefers sp^3 hybridization. The calculated pyramid solid angle on the N atom center (103.6°–103.3°–104.5°) is clearly lower than that on the selected C atom center (109.7°–107.8°–108.5°). The results concerning the adsorption of target cations are reported in Table 1.

The interaction between cations and the surface of NC_{23} is quite different from both of pristine C_{24} and BC_{23} . The adsorption distances from the fullerene surface to the Li^+ , Na^+ , and K^+ ions are 1.82, 2.41 and 2.96 Å, and the E_{in} values are -27.21, -18.67, and -11.30 kcal mol⁻¹, respectively (Fig. 2c and Table 1). However, because of the higher electro-negativity of the nitrogen, when it is doped in C_{24} , charge density of π system in hexagons of the mentioned fullerene reduces as the electron transfer from fullerene to cation does. This phenomenon caused lower E_{in} of alkali ions on the surface of NC_{23} . These data indicate that the order of strength of the cation- π interaction is: $BC_{23} > C_{24} > NC_{23}$. The calculated ν_{cation} values (Table 2) for Li^+ , Na^+ , and K^+ adsorption atop the hexagonal ring of BC_{23} are

300.1, 174.3, and 134.7 cm⁻¹, and those of NC_{23} are 292.3, 163.3, and 154.2 cm⁻¹, respectively. It can be seen that the values of ν_{cation} for cation/ BC_{23} and cation/ NC_{23} complexes are respectively larger and smaller than those of cation/ C_{24} . However, it may be rationalized by the fact that the cation- π interactions in the cation/ BC_{23} are stronger than that of those in cation/ C_{24} , while the cation/ NC_{23} is weaker.

Additionally, we have summarized the results for adsorption of alkali cations atop the center of pentagonal ring in Table 3. In the case of Li^+ adsorption, this cation shifts toward the adjacent C atom during relax optimization; therefore, we have removed its adsorption process because the main goal of the present work was the investigation of cation- π interactions. However, as shown in Table 3, the adsorption of the other two cations atop the pentagonal ring is somewhat less exothermic than that on the hexagonal one (Table 1).

The calculated E_{in} values for Na^+ and K^+ are -20.52 and -12.45 kcal mol⁻¹, respectively. Similar to the case of hexagonal ring, it was found that the adsorption of these cations atop the pentagonal ring slightly increases the E_g of the pristine fullerene from 2.20 eV to 2.28–2.31 eV (Table 1). However, these changes are much smaller than the case of hexagonal ring adsorption, indicating weaker interactions, which are in good agreement with the calculated E_{in} values. As shown in Table 3, compared to the pristine C_{24} , B- and N-doping increase and decrease the E_{in} values, respectively, which is similar to the case of hexagonal ring.

Conclusions

In summary, we have studied the geometrical and electronic structures of the pristine and doped fullerenes of BC_{23} and NC_{23} with and without the presence of alkali cations by performing DFT calculations. It was shown that the most favorable adsorption sites of C_{24} is atop the center of hexagonal ring. The obtained interaction energies of Li^+ , Na^+ and K^+ on the pristine C_{24} are about 31.82, -22.36, and -15.68 kcal mol⁻¹, respectively. We found that the electron tendency of the dopant atom has a large effect on the strength of cation- π interaction. Based on the calculations, when C_{24} has doped with electropositive and electronegative atoms of boron and nitrogen, the interaction energy is increased and decreased, respectively.

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