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Doped hexa-*peri*-hexabenzocoronene as anode materials for lithium- and magnesium-ion batteries†

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The adsorption processes of Li^+ , Li , Mg^{2+} , and Mg on twelve adsorbents (pristine and N/BN/Si-doped hexa-*peri*-hexabenzocoronene (HBC) molecules) were studied using density functional theory. The molecular electrostatic potential (MESP) analyses show that the replacement of C atoms of HBC by N/BN/Si units can provide a more electron-rich system than the parent HBC molecule. Li^+ and Mg^{2+} exhibit strong adsorption on pristine and doped HBC molecules. The adsorption energy of cations on these nanoflakes ($E_{\text{ads-1}}$) was in the range of -247.44 ($\text{Mg}^{2+}/m\text{-C}_{40}\text{H}_{18}\text{N}_2$ system) to -47.65 kcal mol^{-1} ($\text{Li}^+/\text{B}_{21}\text{H}_{18}\text{N}_{21}$ system). Importantly, our results suggest the weaker interactions of Li^+ and Mg^{2+} with the nanoflakes as the MESP minimum values of the nanoflakes became less negative. In all studied systems, we observed electron donation from the nanoflakes to Li^+ and Mg^{2+} . For the metal/nanoflake systems, the adsorption energy of metals on the nanoflakes ($E_{\text{ads-2}}$) was in the range of -33.94 ($\text{Li}/\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$ system) to -2.14 kcal mol^{-1} ($\text{Mg}/\text{B}_{21}\text{H}_{18}\text{N}_{21}$ system). Among the studied anode materials for lithium-ion batteries (LIBs), the highest cell voltage (V_{cell}) of 1.90 V was obtained for $\text{B}_{21}\text{H}_{18}\text{N}_{21}$. Among the studied anode materials for magnesium-ion batteries (MIBs), the highest V_{cell} value of 5.29 V was obtained for $m\text{-C}_{40}\text{H}_{18}\text{N}_2$. $E_{\text{ads-2}}$ has a significant effect on the variation of V_{cell} of LIBs, while $E_{\text{ads-1}}$ has a significant effect on the variation of V_{cell} of MIBs.

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1. Introduction

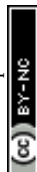
Rechargeable energy storage devices like lithium-ion batteries (LIBs) are in high demand due to their potential applications in electronic devices and electric transportation.^{1–3} Since the commercialization by Sony Corporation in 1991,^{1–3} LIBs have dominated the markets of portable electronic devices and electric vehicles because of their high energy densities and long cycle lives. LIBs are mainly composed of an anode, a cathode, and an electrolyte. Lithium cobalt oxide, lithium iron phosphate, and lithium manganese oxide are typically used as cathode materials for LIBs. The electrolyte of LIBs is mostly based on a lithium salt dissolved in organic solvents. Carbon materials like graphene, carbon nanofibers, carbon nanotubes, polycyclic aromatic hydrocarbons (PAHs), *etc.* have been frequently employed for the construction of anode materials for LIBs.^{4–9} For instance, the high surface areas, electrical

conductivities, and mechanical flexibilities of graphene make it a good candidate for anode materials in LIBs.⁵ Park *et al.* achieved good rate capabilities and cycling stability for LIBs by employing PAH in the design of anode materials.⁷ Arya *et al.* also obtained good cycling stability, high specific capacity, and excellent rate capability for LIBs by employing PAHs in the design of anode materials.⁹ Doped carbon materials have also been employed for the construction of anode materials for LIBs.^{10–13} Recently, divalent metal-ion batteries such as magnesium-ion batteries (MIBs) have attracted considerable interest.^{14,15} Mg could donate two valence electrons and therefore higher storage capacities may be realized in MIBs than in LIBs. Additional features of MIBs such as natural abundance of Mg, lower costs, and good safety make them an excellent alternative to LIBs.¹⁶

PAHs consist of multiple aromatic rings and are rich in delocalized π -electrons. Planar PAHs like coronene, hexa-*peri*-hexabenzocoronene (HBC), and circumcoronene are formed by fusion of 7, 13, and 19 benzene rings, respectively. These planar PAHs may be considered as finite-size models of graphene. Great progress has been made in the design and synthesis of different heteroatom-doped PAHs.^{17–20} For example, the synthesis of HBC with a central borazine core was reported by

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where $G_{\text{adsorbate/nanoflake}}$, $G_{\text{adsorbate}}$, and $G_{\text{nanoflake}}$ denote the free energies of the adsorbed system, adsorbent, and adsorbate, respectively.

The highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gap (E_g) can be calculated using the below equation:

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (4)$$

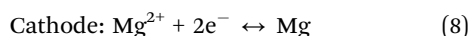
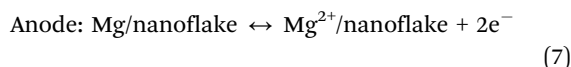
where E_{HOMO} and E_{LUMO} denote the HOMO and LUMO energies, respectively. The E_g of the pristine nanoflake, the $\text{Li}^+/\text{Mg}^{2+}$ -adsorbed nanoflake, and the Li/Mg -adsorbed nanoflake is denoted by E_{g-1} , E_{g-2} , and E_{g-3} , respectively.

The percentage change in the HOMO–LUMO energy gap can be calculated using the below equations:

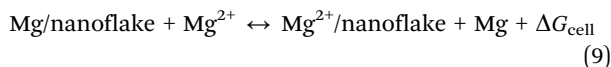
$$\Delta E_{g-1} = [(E_{g-2} - E_{g-1})/E_{g-1}] \times 100 \quad (5)$$

$$\Delta E_{g-2} = [(E_{g-3} - E_{g-1})/E_{g-1}] \times 100 \quad (6)$$

For using a nanoflake as an anode material in, for example, MIBs, the reactions in the anode and cathode can be written as:



Therefore, the total cell reaction is:



The Gibbs free energy change for the total cell reaction (ΔG_{cell}) is described by the following expression:

$$\Delta G_{\text{cell}} = \Delta E_{\text{cell}} + P\Delta V - T\Delta S \quad (10)$$

where

$$\Delta E_{\text{cell}} = E_{\text{ads-1}} - E_{\text{ads-2}} \quad (11)$$

The cell voltage can be calculated using the Nernst equation:

$$V_{\text{cell}} = -\Delta G_{\text{cell}}/zF \quad (12)$$

where F is the Faraday constant ($96485.3 \text{ C mol}^{-1}$) and z is the valence of $\text{Li}^+/\text{Mg}^{2+}$. It might be assumed that $\Delta G_{\text{cell}} \approx \Delta E_{\text{cell}}$, because the contributions of the entropy effect and the volume effect to V_{cell} are expected to be negligible.³⁶

3. Results and discussion

3.1 Doped HBC molecules as anode materials in lithium-ion batteries

3.1.1. Structural properties of doped HBC molecules. Fig. 2 provides the optimized configurations and the relevant bond lengths for the pristine and doped HBC molecules. The XY (X = C, B; Y = C, N, Si) bond lengths in the pristine and doped HBC molecules span from 1.36 to 1.83 Å. The carbon–carbon bond lengths in HBC span from 1.38 to 1.46 Å. This result is in good agreement with the experimental data.³⁷ Clar's aromatic sextet rule can be applied for HBC³⁸ and thus the carbon–carbon

bond length in the central and the six peripheral benzene rings of HBC spans from 1.38 to 1.42 Å. For comparison, the carbon–carbon bond length in benzene is about 1.395 Å.³⁹ In all cases, the carbon–silicon bond lengths ($>1.76 \text{ Å}$) are significantly longer than the carbon–carbon bond lengths.

Table 1 lists the E_{HOMO} , E_{LUMO} , and E_{g-1} values of the pristine and doped HBC molecules. Here the E_{HOMO} , E_{LUMO} , and E_{g-1} values are in the ranges of -8.10 ($\text{B}_{21}\text{H}_{18}\text{N}_{21}$) to -4.01 eV ($m\text{-C}_{40}\text{H}_{18}\text{N}_2$), -1.74 ($\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$) to 0.89 eV ($\text{B}_{21}\text{H}_{18}\text{N}_{21}$), and 2.46 ($m\text{-C}_{40}\text{H}_{18}\text{N}_2$) to 9.00 eV ($\text{B}_{21}\text{H}_{18}\text{N}_{21}$), respectively. The E_{HOMO} , E_{LUMO} , and E_{g-1} values of HBC are -6.39 , -1.00 , and 5.40 eV , respectively. These results are in good agreement with previous theoretical calculations.⁴⁰ Overall, the E_{HOMO} (E_{LUMO}) values of the doped HBC molecules are higher (lower) than those of the pristine HBC. Also, in general, the E_{g-1} values of the doped HBC molecules are lower than those of the pristine HBC. A smaller E_{g-1} value usually indicates a higher electronic conductivity. However, the E_{g-1} values of $\text{C}_{36}\text{H}_{18}\text{B}_3\text{N}_3$ and $\text{B}_{21}\text{H}_{18}\text{N}_{21}$ are higher than those of the pristine HBC.

3.1.2. MESP of doped HBC molecules. Fig. 3 displays the MESP surfaces of the pristine and doped HBC molecules. The MESP plots show the electron-rich region (e.g., green region) on the central and peripheral benzene rings of HBC arising from the cyclic delocalization of π -electrons. Our results show that the replacement of C atoms of HBC by N/BN/Si units can provide a more electron-rich environment (e.g., the blue region). Fig. S1, ESI† provides the location of the MESP V_{min} of the pristine and doped HBC molecules. The MESP V_{min} points were situated near the six peripheral benzene rings of HBC. This indicates the higher electron-richness of the peripheral benzene rings of HBC as compared to the inner rings of HBC. This is due to the fact that the peripheral benzene rings of HBC also have carbon–hydrogen bonds and hydrogen is less electronegative than the sp^2 carbon. Overall, the MESP V_{min} points of all doped HBC molecules were also situated near the peripheral rings. However, the MESP V_{min} points of $o\text{-C}_{40}\text{H}_{18}\text{N}_2$ are situated near the inner N atoms. The MESP V_{min} values of the pristine and doped HBC molecules are listed in Table 1. A higher negative value of MESP V_{min} reflects a more electron rich nature of the nanoflake. These values were in the range of -31.38 ($\text{C}_{28}\text{H}_{18}\text{Si}_{14}$) to $-15.56 \text{ kcal mol}^{-1}$ ($\text{C}_{42}\text{H}_{18}$). A higher negative value of MESP V_{min} reflects a more electron rich nature of the nanoflake. The MESP V_{min} value of the doped HBC molecules was more negative than that of the pristine HBC. In the case of N-doped HBC molecules, the absolute value of MESP V_{min} followed the order $p\text{-C}_{40}\text{H}_{18}\text{N}_2 < o\text{-C}_{40}\text{H}_{18}\text{N}_2 < m\text{-C}_{40}\text{H}_{18}\text{N}_2$. In the case of BN-doped HBC molecules, the absolute value of MESP V_{min} followed the order $\text{C}_{36}\text{H}_{18}\text{B}_3\text{N}_3 < \text{B}_{21}\text{H}_{18}\text{N}_{21} < \text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2 < o\text{-C}_{40}\text{H}_{18}\text{BN} < p\text{-C}_{40}\text{H}_{18}\text{BN} < m\text{-C}_{40}\text{H}_{18}\text{BN}$. The MESP V_{min} value of $\text{C}_{21}\text{H}_{18}\text{Si}_{21}$ ($-28.43 \text{ kcal mol}^{-1}$) was less negative than that of $\text{C}_{28}\text{H}_{18}\text{Si}_{14}$ ($-31.38 \text{ kcal mol}^{-1}$).

3.1.3. Li^+ adsorption on doped HBC molecules. Fig. 4 provides the optimized configurations and the adsorption distances for the adsorption of Li^+ on pristine and doped HBC molecules. We see that Li^+ is bound to the peripheral



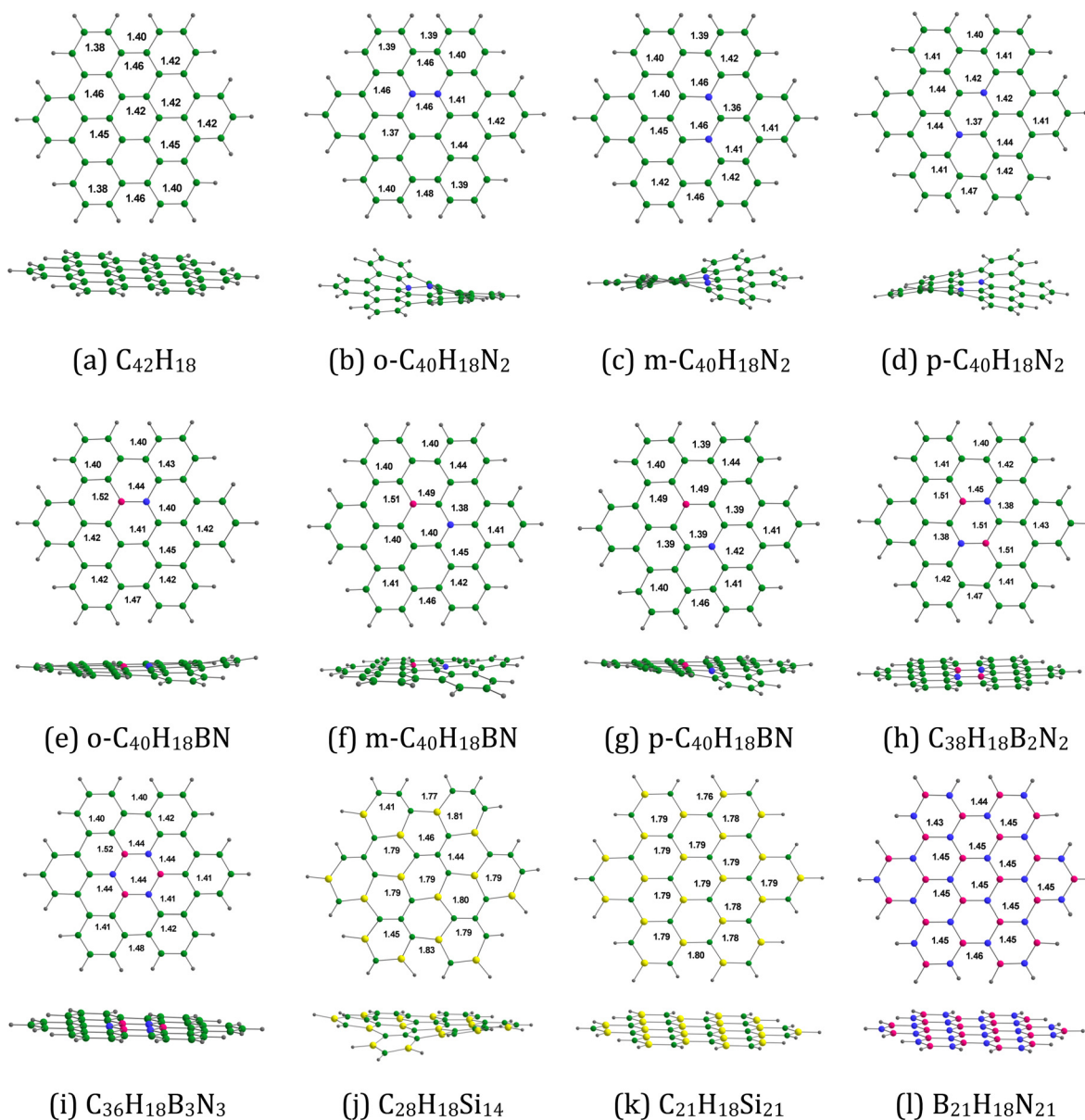


Fig. 2 Optimized structures of (a) $C_{42}H_{18}$, (b) $o\text{-}C_{40}H_{18}N_2$, (c) $m\text{-}C_{40}H_{18}N_2$, (d) $p\text{-}C_{40}H_{18}N_2$, (e) $o\text{-}C_{40}H_{18}BN$, (f) $m\text{-}C_{40}H_{18}BN$, (g) $p\text{-}C_{40}H_{18}BN$, (h) $C_{38}H_{18}B_2N_2$, (i) $C_{36}H_{18}B_3N_3$, (j) $C_{28}H_{18}Si_{14}$, (k) $C_{21}H_{18}Si_{21}$, and (l) $B_{21}H_{18}N_{21}$. The bond distances are given in Å. Color code: green – C, purple – B, blue – N, gray – H, and yellow – Si.

benzene rings of HBC. This is possibly due to the higher electron-richness of the peripheral benzene rings of HBC as compared to the inner rings of HBC (see the above). These adsorption processes involve the cation- π interactions.^{24,41} These interactions are predominantly electrostatic in nature, involving the interaction of Li^+ with the electron cloud of the π -system. Overall, Li^+ is also bound to the peripheral rings of all doped HBC molecules. However, Li^+ is bound to the central ring of $o\text{-}C_{40}H_{18}N_2$. We observe that Li^+ exhibits a relatively strong adsorption on pristine and doped HBC molecules. For instance, the adsorption distances of Li^+ on these nano-flakes span from 2.20 ($Li^+/m\text{-}C_{40}H_{18}N_2$ system) to 2.41 Å ($Li^+/C_{21}H_{18}Si_{21}$ system). The adsorption energy data (Table 2)

also support this possibility. Here the E_{ads-1} values were in the range of -67.34 ($Li^+/C_{28}H_{18}Si_{14}$ system) to -47.65 kcal mol $^{-1}$ ($Li^+/B_{21}H_{18}N_{21}$ system). A higher negative value of E_{ads-1} typically implies a stronger interaction between Li^+ and the nanoflake. The E_{ads-1} value of the Li^+/HBC system was -51.57 kcal mol $^{-1}$. This value is more negative than that of the $Li^+/C_{36}H_{18}B_3N_3$ and $Li^+/B_{21}H_{18}N_{21}$ systems. In the case of Li^+ adsorption on N-doped HBC molecules, the absolute values of E_{ads-1} followed the order $o\text{-}C_{40}H_{18}N_2 < p\text{-}C_{40}H_{18}N_2 < m\text{-}C_{40}H_{18}N_2$. In the case of Li^+ adsorption on BN-doped HBC molecules, the absolute values of E_{ads-1} followed the order $B_{21}H_{18}N_{21} < C_{36}H_{18}B_3N_3 < o\text{-}C_{40}H_{18}BN < C_{38}H_{18}B_2N_2 < p\text{-}C_{40}H_{18}BN < m\text{-}C_{40}H_{18}BN$. The E_{ads-1} value of the $Li^+/C_{21}H_{18}Si_{21}$



Table 1 $V_{\min}$, E_{HOMO} , E_{LUMO} and $E_{\text{g-1}}$ values of doped HBCs^a

Nanoflake	$V_{\min}$	E_{HOMO}	E_{LUMO}	$E_{\text{g-1}}$
$\text{C}_{42}\text{H}_{18}$	−15.56	−6.39	−1.00	5.40
<i>o</i> - $\text{C}_{40}\text{H}_{18}\text{N}_2$	−19.70	−4.89	−1.11	3.78
<i>m</i> - $\text{C}_{40}\text{H}_{18}\text{N}_2$	−24.97	−4.01	−1.55	2.46
<i>p</i> - $\text{C}_{40}\text{H}_{18}\text{N}_2$	−16.44	−4.74	−0.95	3.80
<i>o</i> - $\text{C}_{40}\text{H}_{18}\text{BN}$	−18.64	−6.09	−1.22	4.87
<i>m</i> - $\text{C}_{40}\text{H}_{18}\text{BN}$	−23.41	−5.90	−1.41	4.49
<i>p</i> - $\text{C}_{40}\text{H}_{18}\text{BN}$	−22.53	−6.37	−0.99	5.38
$\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$	−18.14	−5.45	−1.74	3.71
$\text{C}_{36}\text{H}_{18}\text{B}_3\text{N}_3$	−16.32	−6.73	−0.69	6.05
$\text{C}_{28}\text{H}_{18}\text{Si}_{14}$	−31.38	−5.71	−1.71	4.00
$\text{C}_{21}\text{H}_{18}\text{Si}_{21}$	−28.43	−6.44	−1.14	5.30
$\text{B}_{21}\text{H}_{18}\text{N}_{21}$	−17.57	−8.10	0.89	9.00

^a The values are given in eV and $V_{\min}$ in kcal mol^{−1}.

system (−60.82 kcal mol^{−1}) was less negative than that of the $\text{Li}^+/\text{C}_{28}\text{H}_{18}\text{Si}_{14}$ system. Notably, a linear relationship between $E_{\text{ads-1}}$ and MESP $V_{\min}$ values of the nanoflakes exists with a correlation coefficient of 0.913 (Fig. 5a). This finding reflects the weaker interactions of Li^+ with the nanoflakes as the MESP $V_{\min}$ values of the nanoflakes become less negative. For all cases, the adsorption free energies were negative, indicating the spontaneous nature of the adsorption process (see Table 2). Here the $G_{\text{ads-1}}$ values were in the range of −58.02 ($\text{Li}^+/\text{C}_{28}\text{H}_{18}\text{Si}_{14}$ system) to −37.15 kcal mol^{−1} ($\text{Li}^+/\text{B}_{21}\text{H}_{18}\text{N}_{21}$ system).

The electron donation from the nanoflakes to Li^+ can be assessed by determining the MESP at the nucleus of Li^+ before and after adsorption. Therefore, $\Delta V_{\text{MESP-1}}$ is calculated by subtracting the MESP at the nucleus of free Li^+ (−5.36 a.u.) from that of Li^+ in the $\text{Li}^+/\text{nanoflake}$ system. For all cases, the $\Delta V_{\text{MESP-1}}$ values were negative, indicating the electron donation from the nanoflakes to Li^+ (see Table 2). Here the $\Delta V_{\text{MESP-1}}$ values are in the range of −148.34 ($\text{Li}^+/\text{C}_{21}\text{H}_{18}\text{Si}_{21}$ system) to −112.35 kcal mol^{−1} ($\text{Li}^+/\text{C}_{36}\text{H}_{18}\text{B}_3\text{N}_3$ system). The $\Delta V_{\text{MESP-1}}$ value of the Li^+/HBC system is −114.15 kcal mol^{−1}. This value is more negative than that of the $\text{Li}^+/\text{C}_{36}\text{H}_{18}\text{B}_3\text{N}_3$ system. A linear relationship between $E_{\text{ads-1}}$ and $\Delta V_{\text{MESP-1}}$ values exists with a correlation coefficient of 0.863 (Fig. 5b). This finding reflects that stronger interactions of Li^+ with the nanoflakes push more electron density toward Li^+ .

Table 2 also lists the E_{HOMO} , E_{LUMO} , and $E_{\text{g-2}}$ values of the Li^+ -adsorbed nanoflakes. Here the E_{HOMO} , E_{LUMO} , and $E_{\text{g-2}}$ values are in the ranges of −10.45 ($\text{Li}^+/\text{B}_{21}\text{H}_{18}\text{N}_{21}$ system) to −8.24 eV ($\text{Li}^+/\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$ system), −4.62 ($\text{Li}^+/\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$ system) to −3.76 eV ($\text{Li}^+/\text{C}_{21}\text{H}_{18}\text{Si}_{21}$ system), and 2.81 ($\text{Li}^+/\text{m-C}_{40}\text{H}_{18}\text{N}_2$ system) to 6.35 eV ($\text{Li}^+/\text{B}_{21}\text{H}_{18}\text{N}_{21}$ system), respectively. The E_{HOMO} , E_{LUMO} , and $E_{\text{g-2}}$ values of the Li^+/HBC system are −8.98, −4.54, and 4.44 eV, respectively. The E_{HOMO} and E_{LUMO} values of all the Li^+ -adsorbed nanoflakes are lower than those of the corresponding Li^+ -free nanoflakes. In general,

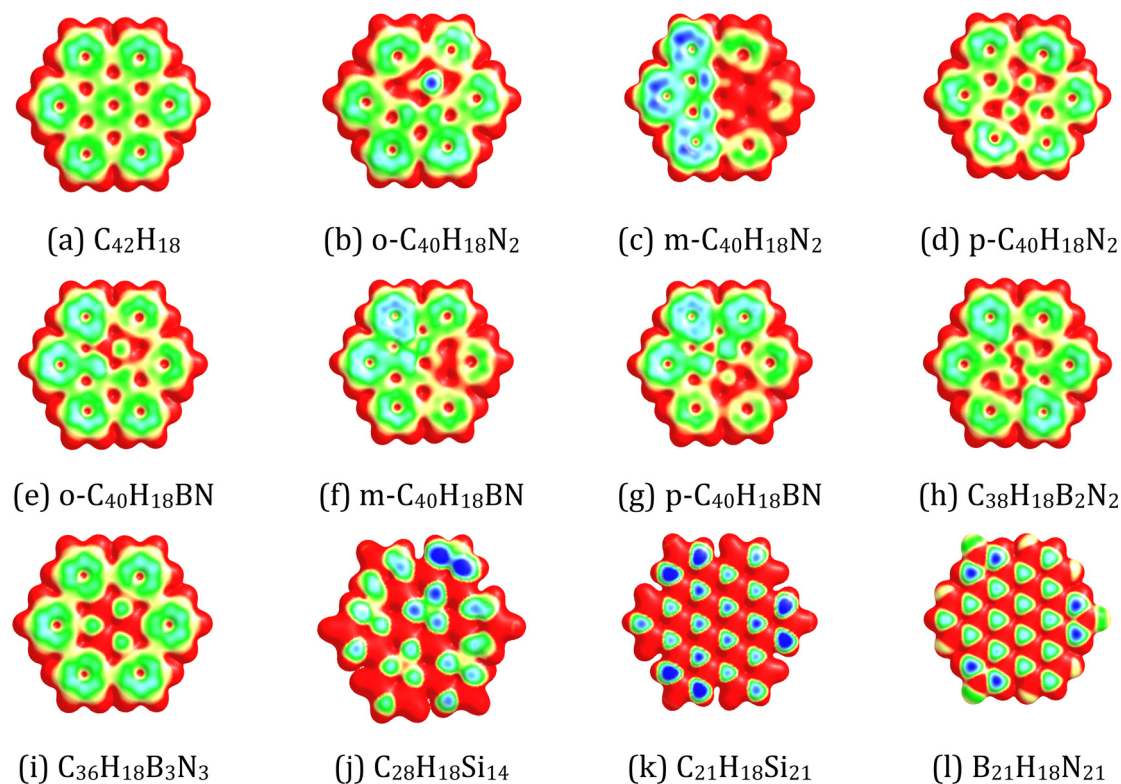


Fig. 3 MESP mapped on the 0.01 a.u. electron density isosurface of (a) $\text{C}_{42}\text{H}_{18}$, (b) *o*- $\text{C}_{40}\text{H}_{18}\text{N}_2$, (c) *m*- $\text{C}_{40}\text{H}_{18}\text{N}_2$, (d) *p*- $\text{C}_{40}\text{H}_{18}\text{N}_2$, (e) *o*- $\text{C}_{40}\text{H}_{18}\text{BN}$, (f) *m*- $\text{C}_{40}\text{H}_{18}\text{BN}$, (g) *p*- $\text{C}_{40}\text{H}_{18}\text{BN}$, (h) $\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$, (i) $\text{C}_{36}\text{H}_{18}\text{B}_3\text{N}_3$, (j) $\text{C}_{28}\text{H}_{18}\text{Si}_{14}$, (k) $\text{C}_{21}\text{H}_{18}\text{Si}_{21}$, and (l) $\text{B}_{21}\text{H}_{18}\text{N}_{21}$. The colour coding from blue to red indicates MESP values in the range −0.03 to 0.03 a.u. The colours at the blue end of the spectrum indicate the electron-rich regions, while those toward the red indicate the electron-deficient regions.



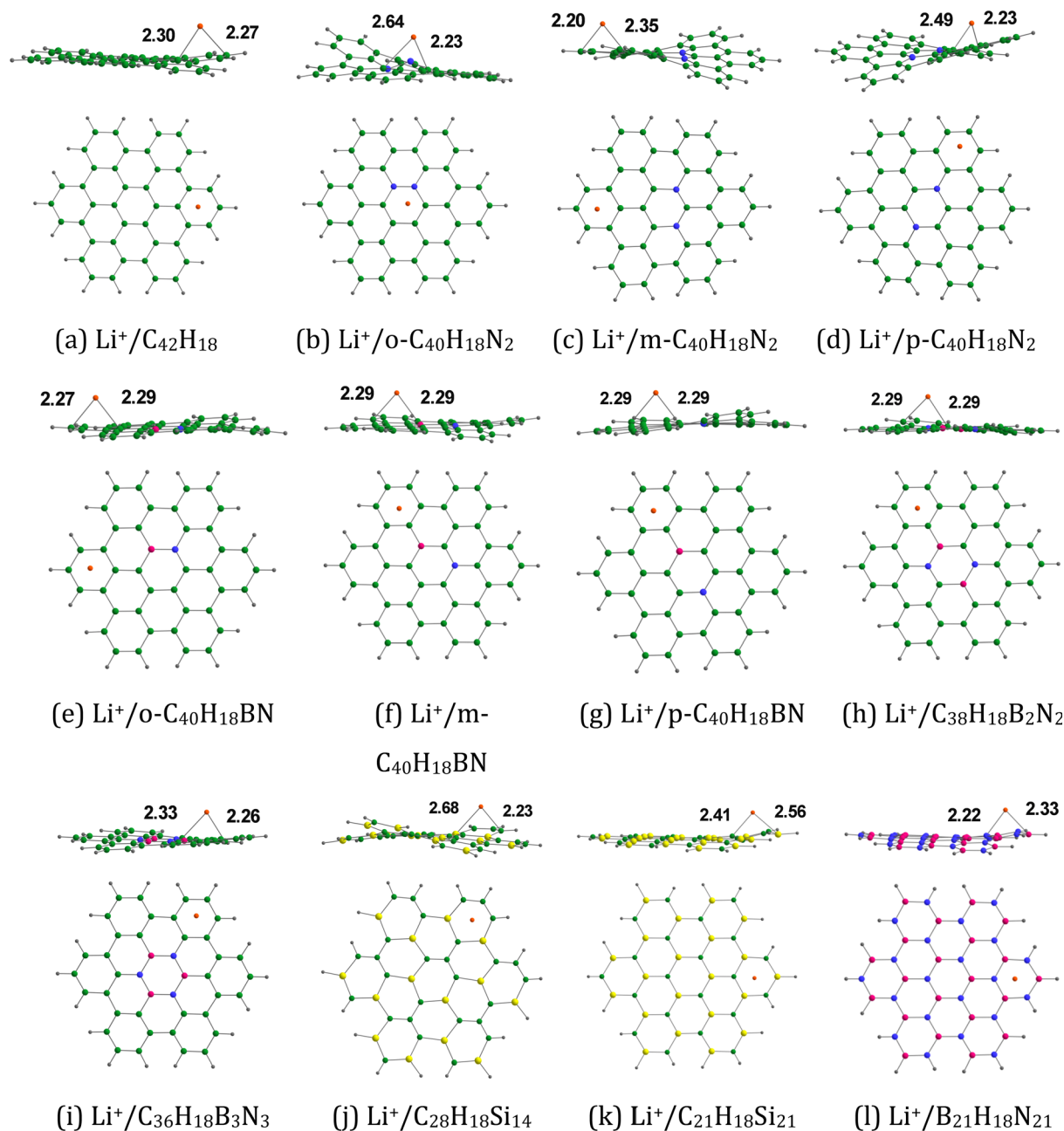


Fig. 4 Optimized structures of Li^+ adsorbed on (a) $\text{C}_{42}\text{H}_{18}$, (b) $\text{o-C}_{40}\text{H}_{18}\text{N}_2$, (c) $\text{m-C}_{40}\text{H}_{18}\text{N}_2$, (d) $\text{p-C}_{40}\text{H}_{18}\text{N}_2$, (e) $\text{o-C}_{40}\text{H}_{18}\text{BN}$, (f) $\text{m-C}_{40}\text{H}_{18}\text{BN}$, (g) $\text{p-C}_{40}\text{H}_{18}\text{BN}$, (h) $\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$, (i) $\text{C}_{36}\text{H}_{18}\text{B}_3\text{N}_3$, (j) $\text{C}_{28}\text{H}_{18}\text{Si}_{14}$, (k) $\text{C}_{21}\text{H}_{18}\text{Si}_{21}$, and (l) $\text{B}_{21}\text{H}_{18}\text{N}_{21}$. The bond distances are given in Å. The color code is the same as in Fig. 2. In addition, Li is denoted by the orange color.

a similar trend was obtained for $E_{\text{g-2}}$. The HOMO–LUMO gap decreased by 17.69% due to Li^+ adsorption on HBC (see the $\Delta E_{\text{g-1}}$ values in Table 2). The maximum decrease in the HOMO–LUMO gap is obtained for Li^+ adsorption on $\text{B}_{21}\text{H}_{18}\text{N}_{21}$ (29.45%). The maximum increase in the HOMO–LUMO gap is obtained for Li^+ adsorption on $\text{m-C}_{40}\text{H}_{18}\text{N}_2$ (14.03%).

3.1.4. Li adsorption on doped HBC molecules. Fig. 6 provides the optimized configurations and the adsorption distances for the adsorption of Li on pristine and doped HBC molecules. Li is mostly bound to the peripheral rings of these nanoflakes, as observed in the case of Li^+ . The adsorption

distances of Li on these nanoflakes span from 2.15 ($\text{Li}/\text{p-C}_{40}\text{H}_{18}\text{N}_2$ system) to 2.25 Å ($\text{Li}/\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$ system). For these nanoflakes, the adsorption distances of Li^+ (see Fig. 4) are typically larger than those of Li. For instance, the adsorption distances of Li^+ and Li on HBC are 2.27 and 2.17 Å, respectively. However, Li^+ was strongly adsorbed on these nanoflakes in comparison with Li. The adsorption energy data (see Tables 2 and 3) support this possibility. Here, the $E_{\text{ads-2}}$ values are in the range of -33.94 ($\text{Li}/\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$ system) to -3.93 kcal mol^{-1} ($\text{Li}/\text{B}_{21}\text{H}_{18}\text{N}_{21}$ system). The $E_{\text{ads-2}}$ value of the Li/HBC system is -17.39 kcal mol^{-1} . This value is more negative than those of

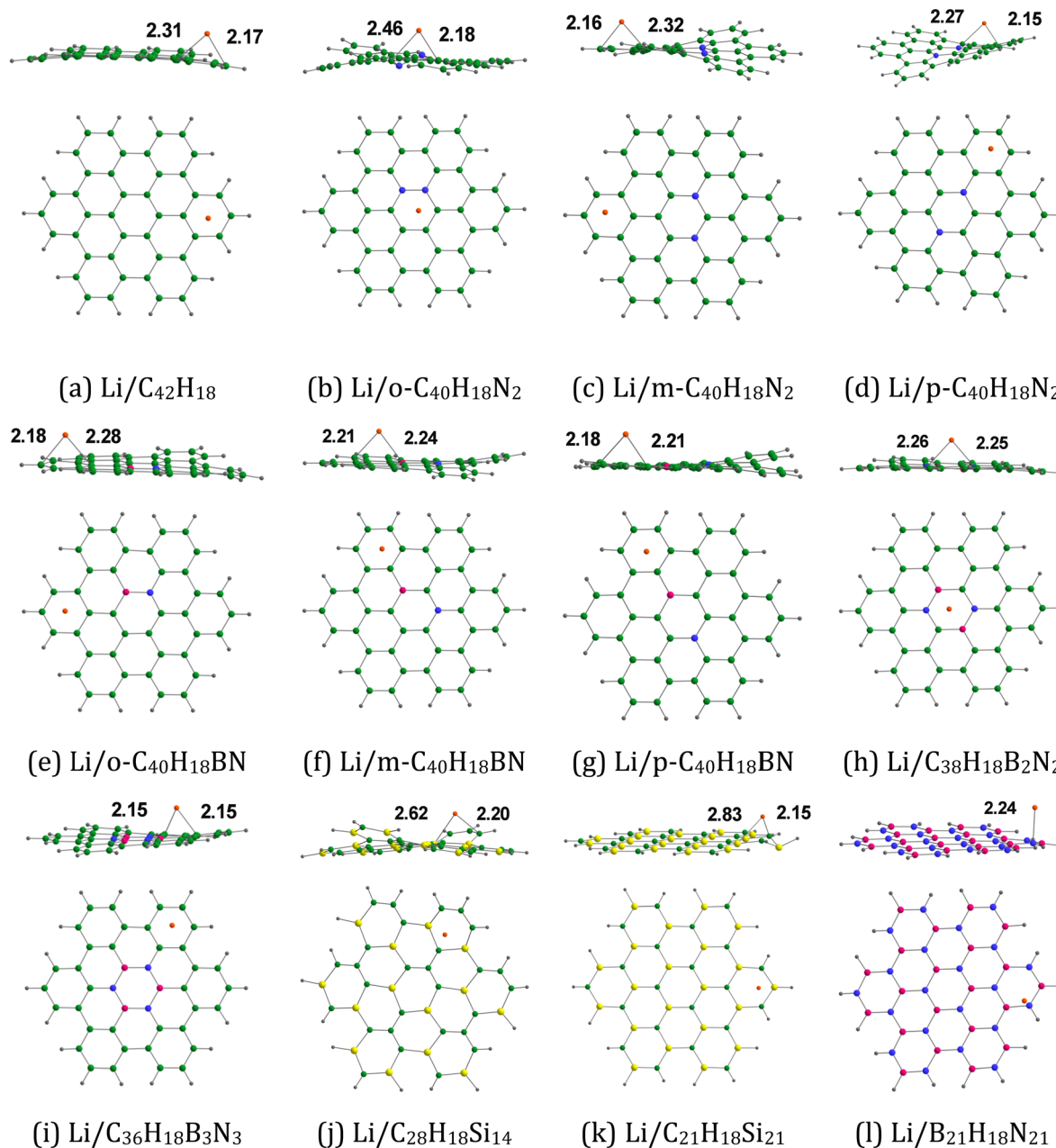


Fig. 6 Optimized structures of Li adsorbed on (a) C₄₂H₁₈, (b) o-C₄₀H₁₈N₂, (c) m-C₄₀H₁₈N₂, (d) p-C₄₀H₁₈N₂, (e) o-C₄₀H₁₈BN, (f) m-C₄₀H₁₈BN, (g) p-C₄₀H₁₈BN, (h) C₃₈H₁₈B₂N₂, (i) C₃₆H₁₈B₃N₃, (j) C₂₈H₁₈Si₁₄, (k) C₂₁H₁₈Si₂₁, and (l) B₂₁H₁₈N₂₁. The bond distances are given in Å. The color code is the same as in Fig. 2. In addition, Li is denoted by the orange color.

C₂₈H₁₈Si₁₄ (1.51 V). When considering all the nanoflakes, unlike $E_{\text{ads-1}}$, $E_{\text{ads-2}}$ shows large variations (see Tables 2 and 3). Thus, $E_{\text{ads-2}}$ can have a significant effect on the variation of V_{cell} . A linear relationship between $E_{\text{ads-2}}$ and V_{cell} with a correlation coefficient of 0.765 further supports the significant effect of $E_{\text{ads-2}}$ on the variation of V_{cell} (Fig. S3a, ESI†).

3.2 HBCs and their analogues as anode materials in magnesium-ion batteries

3.2.1. Mg²⁺ adsorption on doped HBC molecules. Fig. 7 provides the optimized configurations and the adsorption

distances for the adsorption of Mg²⁺ on pristine and doped HBC molecules. We see that Mg²⁺ is bound to the peripheral benzene rings of HBC, similar to the case of Li⁺. Mg²⁺ is also bound to the peripheral rings of all doped HBC molecules except o-C₄₀H₁₈N₂, o-C₄₀H₁₈BN, and p-C₄₀H₁₈N₂. We find that Mg²⁺ is strongly adsorbed on pristine and doped HBC molecules. For instance, the adsorption distances of Mg²⁺ on these nanoflakes span from 3.69 (Mg²⁺/m-C₄₀H₁₈N₂ system) to 2.14 Å (Mg²⁺/B₂₁H₁₈N₂₁ system). The adsorption energy data (Table 4) also support this possibility. Here the $E_{\text{ads-1}}$ values were in the range of −247.44 (Mg²⁺/m-C₄₀H₁₈N₂ system) to



Table 3 $E_{\text{ads-2}}$, $\Delta V_{\text{MESP-2}}$, E_{HOMO} , E_{LUMO} , $E_{\text{g-3}}$ and $\Delta E_{\text{g-2}}$ values of Li adsorbed HBCs, along with ΔE_{cell} and V_{cell} ^a

Nanoflake	$E_{\text{ads-2}}$	$G_{\text{ads-2}}$	$\Delta V_{\text{MESP-2}}$	E_{HOMO}	E_{LUMO}	$E_{\text{g-3}}$	$\Delta E_{\text{g-2}}$	ΔE_{cell}	V_{cell}
C ₄₂ H ₁₈	−17.39	−15.32	16.73	−3.59	−0.98	2.62	−51.51	−34.18	1.48
<i>o</i> -C ₄₀ H ₁₈ N ₂	−23.10	−16.24	14.88	−3.90	−0.88	3.02	−20.22	−29.44	1.28
<i>m</i> -C ₄₀ H ₁₈ N ₂	−30.68	−23.05	20.44	−3.82	−1.04	2.79	13.26	−32.49	1.41
<i>p</i> -C ₄₀ H ₁₈ N ₂	−18.02	−11.74	13.71	−3.64	−0.82	2.82	−25.72	−34.72	1.51
<i>o</i> -C ₄₀ H ₁₈ BN	−20.81	−13.73	16.42	−3.58	−1.02	2.56	−47.43	−34.44	1.49
<i>m</i> -C ₄₀ H ₁₈ BN	−26.64	−19.27	18.51	−3.64	−0.97	2.67	−40.52	−32.66	1.42
<i>p</i> -C ₄₀ H ₁₈ BN	−18.95	−12.63	9.50	−3.35	−1.08	2.27	−57.81	−39.73	1.72
C ₃₈ H ₁₈ B ₂ N ₂	−33.94	−28.74	21.50	−4.39	−0.63	3.76	1.39	−21.66	0.94
C ₃₆ H ₁₈ B ₃ N ₃	−16.40	−13.51	13.21	−3.61	−0.84	2.77	−54.25	−34.40	1.49
C ₂₈ H ₁₈ Si ₁₄	−32.42	−25.10	6.07	−3.73	−1.39	2.34	−41.36	−34.92	1.51
C ₂₁ H ₁₈ Si ₂₁	−30.84	−22.75	−18.32	−4.71	−1.15	3.56	−32.85	−29.98	1.30
B ₂₁ H ₁₈ N ₂₁	−3.93	3.87	−25.98	−3.10	0.32	3.42	−61.99	−43.72	1.90

^a The values of $E_{\text{ads-2}}$, $G_{\text{ads-2}}$, $\Delta V_{\text{MESP-2}}$, and ΔE_{cell} in kcal mol^{−1}; E_{HOMO} , E_{LUMO} , and $E_{\text{g-3}}$ in eV; $\Delta E_{\text{g-2}}$ in %; and V_{cell} in V.

−172.35 kcal mol^{−1} (Mg²⁺/B₂₁H₁₈N₂₁ system). A higher negative value of $E_{\text{ads-1}}$ usually implies a stronger interaction between Mg²⁺ and the nanoflake. The $E_{\text{ads-1}}$ value of the Mg²⁺/HBC system is −178.09 kcal mol^{−1}. This value is more negative than that of the Mg²⁺/C₃₆H₁₈B₃N₃ and Mg²⁺/B₂₁H₁₈N₂₁ systems. In the case of Mg²⁺ adsorption on N-doped HBC molecules, the absolute values of $E_{\text{ads-1}}$ followed the order *o*-C₄₀H₁₈N₂ < *p*-C₄₀H₁₈N₂ < *m*-C₄₀H₁₈N₂. In the case of Mg²⁺ adsorption on BN-doped HBC molecules, the absolute values of $E_{\text{ads-1}}$ followed the order B₂₁H₁₈N₂₁ < C₃₆H₁₈B₃N₃ < *o*-C₄₀H₁₈BN < C₃₈H₁₈B₂N₂ < *p*-C₄₀H₁₈BN < *m*-C₄₀H₁₈BN. The $E_{\text{ads-1}}$ value of the Mg²⁺/C₂₁H₁₈Si₂₁ system (−229.05 kcal mol^{−1}) was less negative than that of the Mg²⁺/C₂₈H₁₈Si₁₄ system (−231.69 kcal mol^{−1}). Here a linear relationship between $E_{\text{ads-1}}$ and MESP V_{min} values of the nanoflakes exists with a correlation coefficient of 0.690 (Fig. 8a). This finding reflects the weaker interactions of Mg²⁺ with the nanoflakes as the MESP V_{min} values of the nanoflakes become less negative. Notably a better correlation was obtained for the adsorption of Li⁺ on pristine and doped HBC molecules (see Fig. 5a). For all cases, the adsorption free energies were negative, indicating the spontaneous nature of the adsorption process (see Table 4). Here the $G_{\text{ads-1}}$ values were in the range of −238.37 (Mg²⁺/*m*-C₄₀H₁₈N₂ system) to −161.41 kcal mol^{−1} (Mg²⁺/B₂₁H₁₈N₂₁ system).

$\Delta V_{\text{MESP-1}}$ is calculated here by subtracting the MESP at the nucleus of free Mg²⁺ (−39.11 a.u.) from that of Mg²⁺ in the Mg²⁺/nanoflake system. For all cases, the $\Delta V_{\text{MESP-1}}$ values were negative, indicating the electron donation from the nanoflakes to Mg²⁺ (see Table 4). Here the $\Delta V_{\text{MESP-1}}$ values are in the range of −387.90 (Mg²⁺/*m*-C₄₀H₁₈N₂ system) to −225.22 kcal mol^{−1} (Mg²⁺/C₃₆H₁₈B₃N₃ system). The $\Delta V_{\text{MESP-1}}$ value of the Mg²⁺/HBC system was −232.55 kcal mol^{−1}. This value is more negative than those of the Mg²⁺/C₃₆H₁₈B₃N₃ and Mg²⁺/B₂₁H₁₈N₂₁ systems. A linear relationship between $E_{\text{ads-1}}$ and $\Delta V_{\text{MESP-1}}$ values exists with a correlation coefficient of 0.829 (Fig. 8b). This finding reflects that stronger interactions of Mg²⁺ with the nanoflakes push more electron density toward Mg²⁺.

Table 4 also lists the E_{HOMO} , E_{LUMO} , and $E_{\text{g-2}}$ values of the Mg²⁺-adsorbed nanoflakes. Here the E_{HOMO} , E_{LUMO} , and $E_{\text{g-2}}$ values are in the ranges of −12.62 (Mg²⁺/B₂₁H₁₈N₂₁ system) to −10.31 eV (Mg²⁺/C₂₁H₁₈Si₂₁ system), −10.02 (Mg²⁺/B₂₁H₁₈N₂₁

system) to −8.05 eV (Mg²⁺/C₂₁H₁₈Si₂₁ system), and 1.35 (Mg²⁺/C₃₆H₁₈B₃N₃ system) to 2.62 eV (Mg²⁺/*p*-C₄₀H₁₈N₂ system), respectively. The E_{HOMO} , E_{LUMO} , and $E_{\text{g-2}}$ values of the Mg²⁺/HBC system are −11.39, −9.74, and 1.65 eV, respectively. The E_{HOMO} and E_{LUMO} values of all the Mg²⁺-adsorbed nanoflakes are lower than those of the corresponding Mg²⁺-free nanoflakes. In general, a similar trend was obtained for $E_{\text{g-2}}$. The HOMO–LUMO gap decreased by 69.35% due to Mg²⁺ adsorption on HBC (see $\Delta E_{\text{g-1}}$ values in Table 4). The maximum decrease in the HOMO–LUMO gap is obtained for Mg²⁺ adsorption on C₃₆H₁₈B₃N₃ (77.60%). However, $E_{\text{g-1}}$ was lower than $E_{\text{g-2}}$ for Mg²⁺ adsorption on *m*-C₄₀H₁₈N₂ ($\Delta E_{\text{g-1}}$ of 5.64%).

3.2.2. Mg adsorption on doped HBC molecules. Fig. 9 provides the optimized configurations and the adsorption distances for the adsorption of Mg on pristine and doped HBC molecules. Mg is mostly bound to the peripheral rings of these nanoflakes, as observed in the case of Mg²⁺. The adsorption distances of Mg on these nanoflakes span from 3.10 (Mg/C₂₈H₁₈Si₁₄ system) to 3.88 Å (Mg/C₂₁H₁₈Si₂₁ system). For these nanoflakes, the adsorption distances of Mg²⁺ (see Fig. 7) are typically smaller than those of Mg. For instance, the adsorption distances of Mg²⁺ and Mg on HBC are 2.30 and 3.61 Å, respectively. Mg²⁺ was strongly adsorbed on these nanoflakes in comparison with Mg. The adsorption energy data (see Tables 4 and 5) support this possibility. Here the $E_{\text{ads-2}}$ values were in the range of −5.11 (Mg/C₂₈H₁₈Si₁₄ system) to −2.14 kcal mol^{−1} (Mg/B₂₁H₁₈N₂₁ system). The $E_{\text{ads-2}}$ value of the Mg/HBC system was −3.17 kcal mol^{−1}. This value is more negative than that of the Mg/C₃₆H₁₈B₃N₃ and Mg/B₂₁H₁₈N₂₁ systems. In the case of Mg adsorption on N-doped HBC molecules, the absolute values of $E_{\text{ads-2}}$ followed the order *p*-C₄₀H₁₈N₂ < *o*-C₄₀H₁₈N₂ < *m*-C₄₀H₁₈N₂. In the case of Mg adsorption on BN-doped HBC molecules, the absolute values of $E_{\text{ads-2}}$ followed the order B₂₁H₁₈N₂₁ < C₃₆H₁₈B₃N₃ < *o*-C₄₀H₁₈BN < *p*-C₄₀H₁₈BN < *m*-C₄₀H₁₈BN < C₃₈H₁₈B₂N₂. The $E_{\text{ads-2}}$ value of the Mg/C₂₁H₁₈Si₂₁ system (−3.58 kcal mol^{−1}) was less negative than that of the Mg/C₂₈H₁₈Si₁₄ system. Here $E_{\text{ads-2}}$ is not well correlated with the MESP V_{min} values of the nanoflakes (Fig. S4, ESI[†]). Overall, the adsorption free energies were positive, suggesting that the adsorption of Mg on nanoflakes is not spontaneous (see Table 5). However, the $G_{\text{ads-2}}$



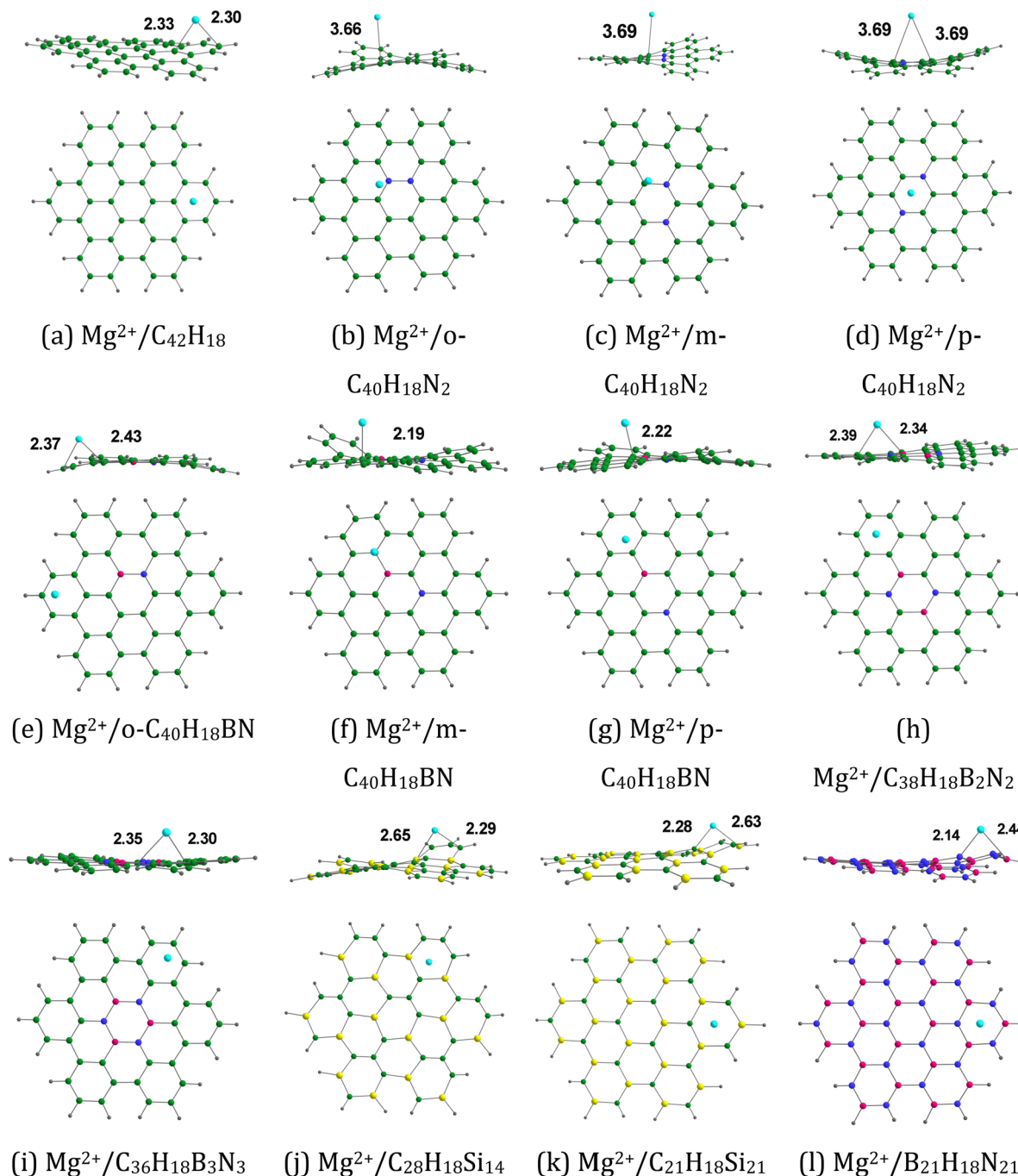


Fig. 7 Optimized structures of Mg^{2+} adsorbed on (a) $\text{C}_{42}\text{H}_{18}$, (b) $o\text{-C}_{40}\text{H}_{18}\text{N}_2$, (c) $m\text{-C}_{40}\text{H}_{18}\text{N}_2$, (d) $p\text{-C}_{40}\text{H}_{18}\text{N}_2$, (e) $o\text{-C}_{40}\text{H}_{18}\text{BN}$, (f) $m\text{-C}_{40}\text{H}_{18}\text{BN}$, (g) $p\text{-C}_{40}\text{H}_{18}\text{BN}$, (h) $\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$, (i) $\text{C}_{36}\text{H}_{18}\text{B}_3\text{N}_3$, (j) $\text{C}_{28}\text{H}_{18}\text{Si}_{14}$, (k) $\text{C}_{21}\text{H}_{18}\text{Si}_{21}$, and (l) $\text{B}_{21}\text{H}_{18}\text{N}_{21}$. The bond distances are given in Å. The color code is the same as in Fig. 2. In addition, Mg is denoted by the cyan color.

values of the $\text{Mg}/\text{C}_{42}\text{H}_{18}$ and $\text{Mg}/\text{C}_{36}\text{H}_{18}\text{B}_3\text{N}_3$ systems are negative, indicating the spontaneous nature of the adsorption process. $\Delta V_{\text{MESP}-2}$ is calculated by subtracting the MESP at the nucleus of free Mg (-39.91 a.u.) from that of Mg in the Mg/nanoflake system. The $\Delta V_{\text{MESP}-2}$ values were negative, indicating the electron donation from the nanoflakes to Mg (see Table 5). Unlike $E_{\text{ads}-1}$, $E_{\text{ads}-2}$ did not display a correlation with $\Delta V_{\text{MESP}-2}$ (see Fig. S4, ESI†).

Table 5 also lists the E_{HOMO} , E_{LUMO} , and $E_{\text{g}-3}$ values of the Mg-adsorbed nanoflakes. Here the E_{HOMO} , E_{LUMO} , and $E_{\text{g}-3}$ values are in the ranges of -5.80 ($\text{Mg}/\text{C}_{21}\text{H}_{18}\text{Si}_{21}$ system) to -4.10 eV ($\text{Mg}/m\text{-C}_{40}\text{H}_{18}\text{N}_2$ system), -1.80 ($\text{Mg}/\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$ system) to 0.12 eV ($\text{Mg}/\text{B}_{21}\text{H}_{18}\text{N}_{21}$ system), and 2.48 ($\text{Mg}/m\text{-C}_{40}\text{H}_{18}\text{N}_2$ system) to 5.88 eV ($\text{Mg}/\text{B}_{21}\text{H}_{18}\text{N}_{21}$ system), respectively. The E_{HOMO} , E_{LUMO} , and $E_{\text{g}-3}$ values of the Mg/HBC system are -5.57 , -1.08 , and 4.49 eV, respectively. Overall, the E_{HOMO} ,

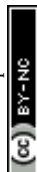


Table 4 $E_{\text{ads-1}}$, $\Delta V_{\text{MESP-1}}$, E_{HOMO} , E_{LUMO} , $E_{\text{g-2}}$ and $\Delta E_{\text{g-1}}$ values of Mg^{2+} adsorbed HBCs^a

Nanoflake	$E_{\text{ads-1}}$	$G_{\text{ads-1}}$	$\Delta V_{\text{MESP-1}}$	E_{HOMO}	E_{LUMO}	$E_{\text{g-2}}$	$\Delta E_{\text{g-1}}$
$\text{C}_{42}\text{H}_{18}$	-178.09	-173.45	-232.55	-11.39	-9.74	1.65	-69.35
$o\text{-C}_{40}\text{H}_{18}\text{N}_2$	-220.45	-213.17	-382.29	-11.00	-8.62	2.38	-37.05
$m\text{-C}_{40}\text{H}_{18}\text{N}_2$	-247.44	-238.37	-387.90	-10.86	-8.26	2.60	5.64
$p\text{-C}_{40}\text{H}_{18}\text{N}_2$	-220.61	-213.27	-371.99	-11.30	-8.68	2.62	-31.09
$o\text{-C}_{40}\text{H}_{18}\text{BN}$	-187.15	-177.46	-254.82	-11.48	-9.64	1.84	-62.28
$m\text{-C}_{40}\text{H}_{18}\text{BN}$	-196.96	-187.18	-267.51	-11.79	-9.31	2.48	-44.70
$p\text{-C}_{40}\text{H}_{18}\text{BN}$	-192.08	-182.61	-239.19	-11.60	-9.50	2.09	-61.14
$\text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2$	-191.56	-183.82	-282.07	-11.12	-9.29	1.83	-50.62
$\text{C}_{36}\text{H}_{18}\text{B}_3\text{N}_3$	-174.18	-168.92	-227.43	-11.32	-9.96	1.35	-77.60
$\text{C}_{28}\text{H}_{18}\text{Si}_{14}$	-231.69	-220.39	-286.89	-10.53	-8.20	2.33	-41.70
$\text{C}_{21}\text{H}_{18}\text{Si}_{21}$	-229.05	-218.53	-294.22	-10.31	-8.05	2.26	-57.34
$\text{B}_{21}\text{H}_{18}\text{N}_{21}$	-172.35	-161.41	-225.22	-12.62	-10.02	2.60	-71.06

^a The values of $E_{\text{ads-1}}$, $G_{\text{ads-1}}$ and $\Delta V_{\text{MESP-1}}$ in kcal mol^{-1} ; E_{HOMO} , E_{LUMO} , and $E_{\text{g-2}}$ in eV; $\Delta E_{\text{g-1}}$ in %.

E_{LUMO} and E_{g} values of all the nanoflakes are not much influenced by the presence of Mg. The HOMO–LUMO gap decreased by 16.73% due to Mg adsorption on HBC (see $\Delta E_{\text{g-2}}$ values in Table 5). The maximum decrease in the HOMO–LUMO gap is obtained for Mg adsorption on $\text{B}_{21}\text{H}_{18}\text{N}_{21}$ (34.65%).

3.2.3. Cell voltage. The ΔE_{cell} and V_{cell} values of MIBs based on the pristine and doped HBC molecules are provided in Table 5. Here the ΔE_{cell} and V_{cell} values were in the ranges of -243.95 ($m\text{-C}_{40}\text{H}_{18}\text{N}_2$) to -170.21 kcal mol^{-1} ($\text{B}_{21}\text{H}_{18}\text{N}_{21}$) and 3.69 ($\text{B}_{21}\text{H}_{18}\text{N}_{21}$) to 5.29 V ($m\text{-C}_{40}\text{H}_{18}\text{N}_2$), respectively. As previously noted, a nanoflake with a strong interaction with Mg^{2+} and a weak interaction with Mg might be regarded as a good candidate for the anode material in metal ion batteries. For instance, in the case of $m\text{-C}_{40}\text{H}_{18}\text{N}_2$, a high V_{cell} value of 5.29 V was obtained because of a high $E_{\text{ads-1}}$ value of -247.44 kcal mol^{-1} (see Table 4) and a low $E_{\text{ads-2}}$ value of -3.50 kcal mol^{-1} (see Table 5). The ΔE_{cell} and V_{cell} values of HBC were -174.91 kcal mol^{-1} and 3.79 V, respectively. In the case of N-doped HBC molecules, the V_{cell} values followed the order $o\text{-C}_{40}\text{H}_{18}\text{N}_2 < p\text{-C}_{40}\text{H}_{18}\text{N}_2 < m\text{-C}_{40}\text{H}_{18}\text{N}_2$. In the case of BN-doped HBC molecules, the V_{cell} values followed the order $\text{B}_{21}\text{H}_{18}\text{N}_{21} < \text{C}_{36}\text{H}_{18}\text{B}_3\text{N}_3 < o\text{-C}_{40}\text{H}_{18}\text{BN} < \text{C}_{38}\text{H}_{18}\text{B}_2\text{N}_2 <$

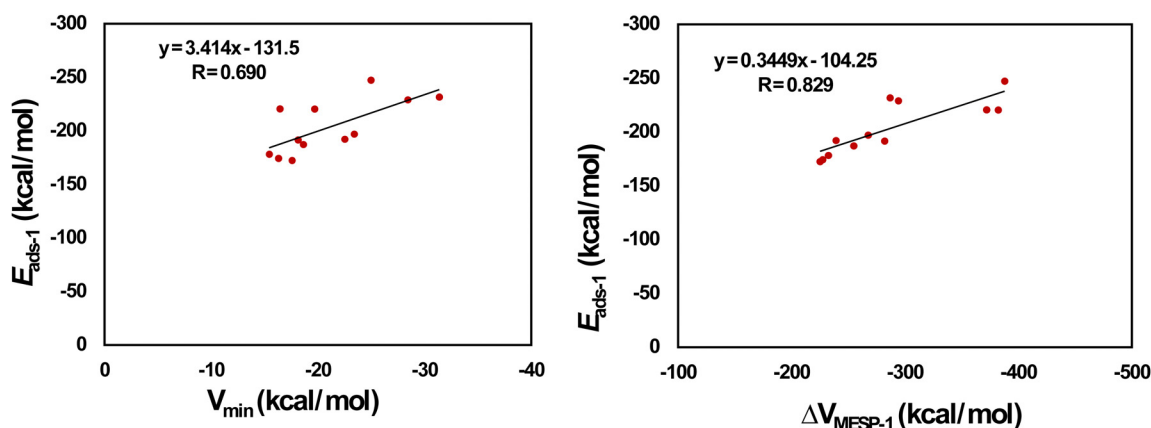
$p\text{-C}_{40}\text{H}_{18}\text{BN} < m\text{-C}_{40}\text{H}_{18}\text{BN}$. The V_{cell} value of $\text{C}_{21}\text{H}_{18}\text{Si}_{21}$ (4.89 V) was slightly lower than that of $\text{C}_{28}\text{H}_{18}\text{Si}_{14}$ (4.91 V). When considering all the nanoflakes, unlike $E_{\text{ads-2}}$, $E_{\text{ads-1}}$ shows large variations (see Tables 4 and 5). Thus, here, $E_{\text{ads-1}}$ can have a significant effect on the variation of V_{cell} . A strong linear relationship between $E_{\text{ads-1}}$ and V_{cell} further supports the significant effect of $E_{\text{ads-1}}$ on the variation of V_{cell} (see Fig. S3b, ESI†).

The changes in E_{g} could influence the electrical conductivity (σ) of the material. The relationship between σ and E_{g} is given as:⁴²

$$\sigma \propto \exp(-E_{\text{g}}/2kT)$$

where k is the Boltzmann constant and T is the temperature. Our results show that the $E_{\text{g-1}}$ values of the doped HBC molecules are lower than those of the pristine HBC. A smaller $E_{\text{g-1}}$ value indicates a higher electronic conductivity. Furthermore, the E_{g} values of the cation/metal-adsorbed nanoflakes were usually lower than those of the cation/metal-free nanoflakes.

The MESP is a real physical property which can be determined using X-ray diffraction techniques or computational methods. The MESP analyses showed that the replacement of the C atoms of HBC by N/BN/Si units provides a more electron-rich system than the parent HBC molecule. Importantly, we observed stronger interactions of Li^+ and Mg^{2+} with the nanoflakes as the MESP minimum values of the nanoflakes became more negative. We observed weaker interactions of Li^+ and Mg^{2+} with the nanoflakes as the MESP minimum values of the nanoflakes become less negative. The adsorption energy of Li has a significant effect on the variation of V_{cell} of LIBs, while the adsorption energy of Mg^{2+} has a significant effect on the variation of V_{cell} of MIBs. Furthermore, the storage capacity ($C = (n \times z \times F \times 10^3)/M$, where n is the maximum number of adsorbed metal atoms and M is the molecular mass of the electrode) is an important factor for the performance of metal-ion batteries.²³ Such nanoflakes are promising anode materials for high-capacity metal-ion batteries. For example, the lithium storage capacity of coronene was 536.2 mA h g^{-1} and the magnesium storage capacity of HBC was 923.1 mA h g^{-1} .^{23,27}

**Fig. 8** Correlation between (a) V_{min} and $E_{\text{ads-1}}$ (b) $\Delta V_{\text{MESP-1}}$ and $E_{\text{ads-1}}$ for Mg^{2+} -adsorbed HBCs.

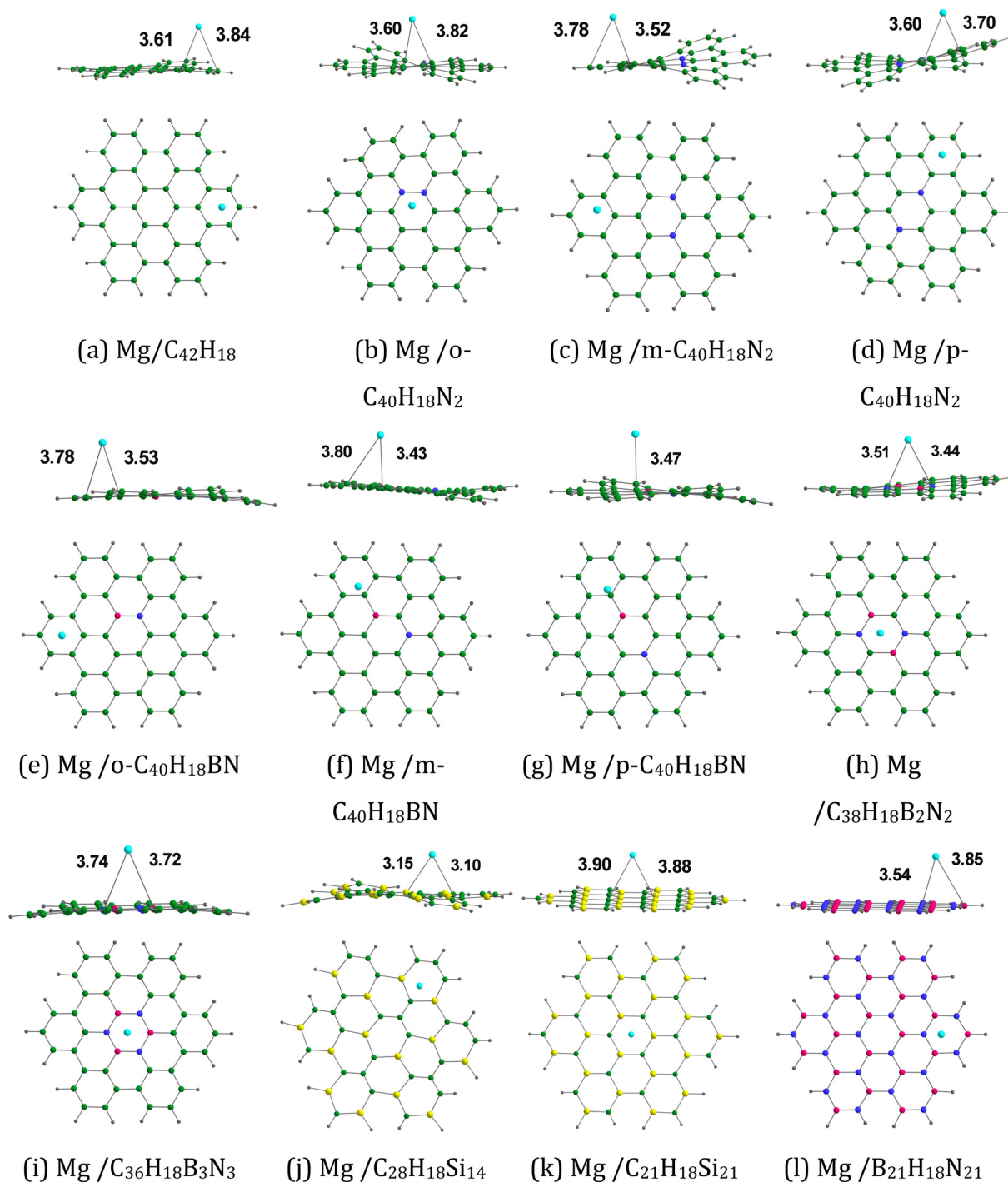


Fig. 9 Optimized structures of Mg adsorbed on (a) $C_{42}H_{18}$, (b) o - $C_{40}H_{18}N_2$, (c) m - $C_{40}H_{18}N_2$, (d) p - $C_{40}H_{18}N_2$, (e) o - $C_{40}H_{18}BN$, (f) m - $C_{40}H_{18}BN$, (g) p - $C_{40}H_{18}BN$, (h) $C_{38}H_{18}B_2N_2$, (i) $C_{36}H_{18}B_3N_3$, (j) $C_{28}H_{18}Si_{14}$, (k) $C_{21}H_{18}Si_{21}$, and (l) $B_{21}H_{18}N_{21}$. The bond distances are given in Å. The color code is the same as in Fig. 2. In addition, Mg is denoted by the cyan color.

For a comparison, the lithium storage capacity of graphite is 372 mA h g^{-1} , that of Sc₂C MXene is 462 mA h g^{-1} , that of graphene-like C_2N is $671.7 \text{ mA h g}^{-1}$, and that of pentagraphyne is 687 mA h g^{-1} .²³ This work could provide insights into the design and exploration of anode materials suitable for metal ion batteries.

The doping process and/or the adsorption process could affect the planar structure of the HBC molecule. The formation

of non-planar structures is more evident in o - $C_{40}H_{18}N_2$, m - $C_{40}H_{18}N_2$, and p - $C_{40}H_{18}N_2$ (see Fig. 2) and Mg^{2+} -adsorbed nanoflakes (see Fig. 7). The diffusion of $Li^+/Li/Mg^{2+}/Mg$ on the nanoflake surface could be an important factor for battery applications.⁴³ For example, the lower diffusion barrier of Li^+ accelerates the charging and discharging process of the battery.⁴³ We plan to study the diffusion processes in a future publication.



Table 5 $E_{\text{ads-2}}$, $\Delta V_{\text{MESP-2}}$, E_{HOMO} , E_{LUMO} , $E_{\text{g-3}}$ and $\Delta E_{\text{g-2}}$ values of Mg adsorbed HBCs, along with ΔE_{cell} and V_{cell} ^a

Nanoflake	$E_{\text{ads-2}}$	$G_{\text{ads-2}}$	$\Delta V_{\text{MESP-2}}$	E_{HOMO}	E_{LUMO}	$E_{\text{g-3}}$	$\Delta E_{\text{g-2}}$	ΔE_{cell}	V_{cell}
C ₄₂ H ₁₈	−3.17	−0.65	−12.38	−5.57	−1.08	4.49	−16.73	−174.91	3.79
<i>o</i> -C ₄₀ H ₁₈ N ₂	−3.37	2.21	−12.13	−4.95	−1.18	3.77	−0.29	−217.08	4.71
<i>m</i> -C ₄₀ H ₁₈ N ₂	−3.50	2.56	−18.73	−4.10	−1.62	2.48	0.66	−243.95	5.29
<i>p</i> -C ₄₀ H ₁₈ N ₂	−3.34	2.94	−11.96	−4.83	−1.03	3.80	0.07	−217.27	4.71
<i>o</i> -C ₄₀ H ₁₈ BN	−3.20	3.03	−14.90	−5.45	−1.31	4.14	−15.01	−183.95	3.99
<i>m</i> -C ₄₀ H ₁₈ BN	−3.61	2.58	−17.56	−5.30	−1.50	3.80	−15.38	−193.36	4.19
<i>p</i> -C ₄₀ H ₁₈ BN	−3.48	2.93	−17.12	−5.33	−1.09	4.24	−21.27	−188.60	4.09
C ₃₈ H ₁₈ B ₂ N ₂	−4.73	0.07	−9.53	−5.54	−1.80	3.74	0.81	−186.83	4.05
C ₃₆ H ₁₈ B ₃ N ₃	−2.57	−2.06	−7.58	−5.74	−0.71	5.03	−16.82	−171.62	3.72
C ₂₈ H ₁₈ Si ₁₄	−5.11	1.81	−10.95	−5.00	−1.76	3.24	−18.98	−226.58	4.91
C ₂₁ H ₁₈ Si ₂₁	−3.58	1.95	−3.77	−5.80	−1.15	4.65	−12.27	−225.46	4.89
B ₂₁ H ₁₈ N ₂₁	−2.14	3.89	−7.07	−5.76	0.12	5.88	−34.65	−170.21	3.69

^a The values of $E_{\text{ads-2}}$, $G_{\text{ads-2}}$, $\Delta V_{\text{MESP-2}}$, and ΔE_{cell} in kcal mol^{−1}; E_{HOMO} , E_{LUMO} , and $E_{\text{g-3}}$ in eV; $\Delta E_{\text{g-2}}$ in %; and V_{cell} in V.

4. Conclusions

DFT studies were carried out to understand the adsorption process of Li⁺, Li, Mg²⁺, and Mg on twelve adsorbents (pristine and N/BN/Si-doped HBC molecules C₄₂H₁₈, *o*-C₄₀H₁₈N₂, *m*-C₄₀H₁₈N₂, *p*-C₄₀H₁₈N₂, *o*-C₄₀H₁₈BN, *m*-C₄₀H₁₈BN, *p*-C₄₀H₁₈BN, C₃₈H₁₈B₂N₂, C₃₆H₁₈B₃N₃, C₂₈H₁₈Si₁₄, C₂₁H₁₈Si₂₁, and B₂₁H₁₈N₂₁). The XY (X = C, B; Y = C, N, Si) bond lengths in the pristine and doped HBC molecules span from 1.36 to 1.83 Å. In all cases, the carbon–silicon bond lengths (> 1.76 Å) are significantly longer than the carbon–carbon bond lengths. The MESP analyses show that the replacement of C atoms of HBC by N/BN/Si units can provide a more electron-rich system than the parent HBC molecule.

Li⁺ exhibits a relatively strong adsorption on pristine and doped HBC molecules. The adsorption distances of Li⁺ on these nanoflakes span from 2.20 (*m*-C₄₀H₁₈N₂) to 2.41 Å (C₂₁H₁₈Si₂₁). Here the $E_{\text{ads-1}}$ values were in the range of −67.34 (Li⁺/C₂₈H₁₈Si₁₄ system) to −47.65 kcal mol^{−1} (Li⁺/B₂₁H₁₈N₂₁ system). For the Li/nanoflake system, the $E_{\text{ads-2}}$ values were in the range of −33.94 (Li/C₃₈H₁₈B₂N₂ system) to −3.93 kcal mol^{−1} (Li/B₂₁H₁₈N₂₁ system). Mg²⁺ also exhibits a relatively strong adsorption on the pristine and doped HBC molecules. Here the $E_{\text{ads-1}}$ values were in the range of −247.44 (Mg²⁺/*m*-C₄₀H₁₈N₂ system) to −172.35 kcal mol^{−1} (Mg²⁺/B₂₁H₁₈N₂₁ system). Our results suggest the weaker interactions of Li⁺ and Mg²⁺ with the nanoflakes as the MESP V_{min} values of the nanoflakes become less negative. In all studied systems, we found electron donation from the nanoflakes to Li⁺ and Mg²⁺. For the Mg/nanoflake system, the $E_{\text{ads-2}}$ values were in the range of −5.11 (Mg/C₂₈H₁₈Si₁₄ system) to −2.14 kcal mol^{−1} (Mg/B₂₁H₁₈N₂₁ system). The HOMO–LUMO gap of the cation/metal-adsorbed nanoflakes was usually lower than that of the cation/metal-free nanoflakes.

A nanoflake with a strong interaction with Li⁺/Mg²⁺ and a weak interaction with Li/Mg might be regarded as a good candidate for the anode material in metal ion batteries. Among the studied anode materials for LIBs, the highest V_{cell} value of 1.90 V was obtained for B₂₁H₁₈N₂₁ because of the high $E_{\text{ads-1}}$ value of −47.65 kcal mol^{−1} and the low $E_{\text{ads-2}}$ value of −3.93 kcal mol^{−1}. Among the studied anode materials for MIBs,

the highest V_{cell} value of 5.29 V was obtained for *m*-C₄₀H₁₈N₂ because of the high $E_{\text{ads-1}}$ value of −247.44 kcal mol^{−1} and the low $E_{\text{ads-2}}$ value of −3.50 kcal mol^{−1}. For LIBs, $E_{\text{ads-2}}$ has a significant effect on the variation of V_{cell} , while for MIBs, $E_{\text{ads-1}}$ has a significant effect on the variation of V_{cell} .

Data availability

The data that support the findings of this study are available upon request from the corresponding author.

Conflicts of interest

There are no conflicts to declare.

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