

**EXPLORING THE POTENTIAL OF CONDUCTING POLYMER-
FUNCTIONALIZED BORON-BASED 2D NANOSHEETS TO
DESIGN A NEW GENERATION OF METAL-ION BATTERIES:
A FIRST-PRINCIPLES STUDY**

BY

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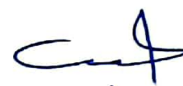
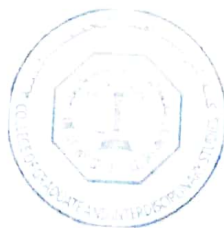


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2025

DEDICATION

This project is solely dedicated to my beloved mother, whose unwavering support and unconditional love have been the driving force behind my academic journey, and in gratitude for being my guiding light and source of inspiration. May Allah SWT reward her with Jannatul-Firdaus.

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LIST OF ABBREVIATIONS

BCNNS	:Boron Carbon Nitride Nanosheet
BIB	:Beryllium-ion Battery
BNNC	:Boron Nitride Nanocage
BNNS	:Boron Nitride Nanosheet
Ca₂N	:Calcium nitride
C_m	:Specific Capacity
CP	:Conducting Polymer
CVD	:Chemical Vapor Deposition
DFT	:Density Functional Theory
DMF	:Dimethylformamide
DNP	:Double Numerical polarization
EDG	:Electron Withdrawing Group
EES	:Electrochemical Energy Storage
EWG	:Electron Donating Group
GGA	:Generalized Gradient Approximation
h-BCN	:Hexagonal Boron Carbon Nitride
h-BN	:Hexagonal Boron nitride
HOMO	:Highest Occupied Molecular Orbital
HSAB	:Hard/Soft Acid/Base
LIB	:Lithium-ion Battery
LUMO	:Lowest Unoccupied Molecular Orbital
MIB	:Magnesium-ion Battery
Mo₂C	:Molybdenum Carbide
MoS₂	:Molybdenum disulfide
MoSe₂	:Molybdenum diselenide
Nb₂C	:Niobium Carbide
OCV	:Open Circuit Voltage

PA	:Poly Acetylene
PANI	:Polyaniline
PBE	:Perdew-Burke-Ernzerhof
pp	:Poly Pyrrole
PPPh	:Poly Para Phenylene
PT	:Poly Thiophene
SCF	:Self-consistent field
SEI	:Solid Electrolyte Interface
SIB	:Sodium-ion Battery
SnS₂	:Tin disulfide
TDOS	:Total Density of States
TiC₂	:Titanium Carbide
TiN	:Titanium nitride
TiS₂	:Titanium disulfide
TMDs	:Transition Metals Dichalcogenides
UV	:Ultraviolet
V₂C	:Vanadium Carbide
VN	:Vanadium nitride
VS₂	:Vanadium Sulfide
WS₂	:Tungsten disulfide

ABSTRACT

Full Name : SHEHU MOHAMMED

Thesis Title : EXPLORING THE POTENTIAL OF CONDUCTING POLYMER-FUNCTIONALIZED BORON-BASED 2D NANOSHEETS TO DESIGN A NEW GENERATION OF METAL-ION BATTERIES: A FIRST-PRINCIPLES STUDY

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Lithium-ion batteries (LIBs) have long dominated rechargeable energy storage due to their superior performance. Yet, there is ample opportunity for further innovation, particularly in developing cost-effective, high-energy, and lightweight materials for advanced anodes. Thus, fabricating anodic materials with low diffusion barriers and optimal cell voltage is essential for enhancing the efficiency of secondary batteries. This study utilizes first-principles Density Functional Theory (DFT) simulations to investigate how conducting polymer-functionalized two-dimensional boron nitride nanosheets (BNNS), boron carbon nitride nanocage and fullerene-like $B_{12}N_{12}$ nanocage can enhance the performance of metal-ion batteries. We explored the role of poly-p-phenylene (PPPh) functionalization in improving the anodic properties of boron nitride (BN) and (BCN) nanosheets and further examined the influence of various electron-donating and electron-withdrawing substituents such as hydroxyl, amino, cyano, methyl, methoxy, chloro, bromo fluoro, carboxyl, and nitro groups on the conducting polymer-functionalized two-dimensional hybrid materials for potential use in lithium, sodium, beryllium, and magnesium-ion batteries. On the other hand, the impact of various conducting polymers (CPs), namely polyacetylene (PA), poly-para-phenylene (PPPh), polypyrrole (PP), and polythiophene (PT) was

investigated on the electronic features and anodic efficiency of fullerene-like $B_{12}N_{12}$ nanocage towards the design of lithium and sodium-ion batteries.

The functionalization of the various conducting polymers significantly altered and improved the structural, electrical, and thermal stabilities of the 2D BNNS, BCNNS, and fullerene-like $B_{12}N_{12}$.

Notably, coupling BNNS with nitro-substituted PPPh resulted in a 63% reduction in the HOMO-LUMO energy gap and a significant cell voltage enhancement, with predicted voltages reaching 3.66 V for Li-ion, 3.18 V for Na-ion, 3.14 V for Be-ion, and 6.89 V for Mg-ion batteries. In addition, a theoretical specific capacity of 244 and 217 mAh/g was recorded for the designed LIBs and SIBs respectively.

Similarly, the electronic properties of BCNNS were tuned through functionalization with PPPh-conducting polymer. Furthermore, the effects of various EWG and EDG on the PPPh-BCNNS resulted in improved electronics and structural properties of the complex material. The bromo-PPPh functionalized BCNNS shows the most promising potential with an increased in band gap of 14% when compared to the pristine nanosheet. The enhanced properties led to improve in predicted cell voltages of 2.62 V for Li-ion, 2.59 V for Na-ion, 8.20 V for Be-ion, and 6.02 V for Mg-ion batteries.

The functionalization of $B_{12}N_{12}$ with of various conducting polymers (CPs), namely polyacetylene (PA), poly-para-phenylene (PPPh), polypyrrole (PP), and polythiophene (PT) resulted in improved cell reaction kinetics and charge transfer properties as a result of molecular orbitals stabilization. Notably, reduction in the

energy gaps of approximately 90% for PA, 42% for PPPh, 51% for PP, and 61% for PT was predicted. While the cell voltage of bare B₁₂N₁₂ nanocage was predicted to be 0.98 V for Li⁺ and 1.20 V for Na⁺ ions, the functionalization with various CPs lead to a notable enhancement in cell voltages (up to 4.14 V for Li⁺ and 3.98 V for Na⁺ ions). This study highlights the critical influence of functional group chemistry, impact of metal ion size and electronic density, structural characteristics of the interfacing conducting polymer and metal-ion properties in optimizing battery efficiency. Our findings offer a DFT-driven framework for the rational design of next-generation metal-ion batteries, emphasizing the strategic use of functionalized BNNS, BCNNS and fullerene-like B₁₂N₁₂ nanocage for superior energy storage solutions.

ملخص الرسالة

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هيمنت لفترة طويلة على تخزين الطاقة القابلة لإعادة الشحن بسبب (LIBs) البطاريات القائمة على أيون الليثيوم أدائها المتفوق. ومع ذلك، هناك مجال واسع لمزيد من الابتكار، خاصة في تطوير مواد الأنود المتقدمة التي تتميز بكونها منخفضة التكلفة، وعالية الطاقة، وخفيفة الوزن. لذا، فإن تصنيع مواد أنودية ذات حواجز انتشار منخفضة. وجهد خلية مثالي يعد أمرًا ضروريًا لتحسين كفاءة البطاريات الثانوية.

من المبادئ الأولى لدراسة كيفية تعزيز أداء بطاريات (DFT) تستخدم هذه الدراسة محاكاة نظرية الكثافة الوظيفية معالجة ببولىميرات (BNNS) أيونات المعادن من خلال استخدام صفائح نانوية ثنائية الأبعاد من نيتريد البورون B12N12. وبني تشبه الفوليرين من (BCN) موصلة، بالإضافة إلى أقفاص نانوية من بورون-كربون-نيتروجين (BN) في تحسين الخصائص الأنودية لصفائح نيتريد البورون (PPPh) قمنا بدراسة دور تعديل البولي-بارا-فينيلين، النانوية، كما فحصنا تأثير مجموعات مائحة للإلكترونات وساحبة لها، مثل الهيدروكسيل، الأمينو (BCN) والسيانو، الميثيل، الميثوكسي، الكلورو، البرومو، الفلورو، الكربوكسيل، والنيترو على المواد الهجينة الثنائية الأبعاد الوظيفية، لاستخدامها المحتمل في بطاريات أيونات الليثيوم، الصوديوم، البيريلىوم، والمغنيسيوم.

البولي- (PA) وهي البولي أسيتيلين (CPS) من ناحية أخرى، تم التحقيق في تأثير البولىميرات الموصلة المختلفة على الخصائص الإلكترونية والكفاءة الأنودية (PT) والبولى ثيوفين (PP) البولى بيرول (PPPh) بارا-فينيلين الشبيه بالفوليرين، بهدف تصميم بطاريات أيونات الليثيوم والصوديوم B12N12 للقفص النانوي.

أدى تعديل البولىميرات الموصلة المختلفة إلى تحسينات كبيرة في الاستقرار الهيكلي، الكهربائي، والحراري لصفائح المستبدل PPPh مع BNNS ومن الجدير بالذكر أن اقتران B12N12 والقفص النانوي، BCNNS، BNNS بنسبة 63% وتحسين كبير في جهد الخلية، حيث HOMO-LUMO بالنيترو أدى إلى تقليل فجوة الطاقة بين وصلت القيم المتوقعة إلى 3.66 فولت لبطاريات أيون الليثيوم، 3.18 فولت لبطاريات أيون الصوديوم، 3.14 فولت لبطاريات أيون البيريلىوم، و6.89 فولت لبطاريات أيون المغنيسيوم. بالإضافة إلى ذلك، تم تسجيل سعة نوعية نظرية على التوالي LIBs وSIBs بلغت 244 و217 ملي أمبير/غرام للبطاريات المصممة من نوع.

الموصل. كما أدى تأثير PPPh من خلال تعديلها ببولىمير BCNNS وبالمثل، تم ضبط الخصائص الإلكترونية لـ إلى تحسين الخصائص الإلكترونية والهيكلية PPPh-BCNNS المجموعات الساحبة والمائحة للإلكترونات على المستبدل بالبرومو إمكانية واحدة، حيث زادت فجوة PPPh المعدلة بـ BCNNS للمادة المركبة. وقد أظهرت الطاقة بنسبة 14% مقارنة بالصفائح النانوية غير المعدلة، مما أدى إلى تحسين جهد الخ

لية إلى 2.62 فولت لأيون الليثيوم، 2.59 فولت لأيون الصوديوم، 8.20 فولت لأيون البيريليوم، و6.02 فولت لأيون المغنيسيوم.

أدى إلى تحسين PT، وPP، PPPh، PA بأنواع مختلفة من البوليمرات الموصلة، مثل B12N12 كما أن تعديل ديناميكيات التفاعل داخل الخلية وخصائص نقل الشحنة نتيجة لاستقرار المدارات الجزيئية. ومن الجدير بالذكر أن في PT. و61% لـ PP، و51% لـ PPPh، و42% لـ PA، تقليل فجوات الطاقة المتوقعة بلغ حوالي 90% لـ غير المعدل بـ 0.98 فولت لأيون الليثيوم و1.20 فولت لأيون B12N12 حين تم توقع جهد الخلية للقفص النانوي الصوديوم، أدى التعديل باستخدام البوليمرات الموصلة المختلفة إلى تحسينات ملحوظة في جهود الخلايا (حتى 4.14 فولت لـ Na+ و3.98 فولت لـ Li+ فولت لـ).

تُبرز هذه الدراسة التأثير الحاسم للكيمياء الوظيفية للمجموعات المستبدلة، وحجم أيونات المعادن، والكثافة الإلكترونية، والخصائص الهيكلية للبوليمر الموصل البيني، وتأثير أيونات المعادن في تحسين كفاءة البطارية. وتقدم لتصميم بطاريات أيونات المعادن من الجيل القادم بشكل منهجي، مع التركيز على DFT نتائجا إطارًا قائمًا على الشبيه بالفوليرين B12N12 والقفص النانوي، BNNS، BCNNS الاستخدام الاستراتيجي للمواد الوظيفية لتحقيق حلول تخزين طاقة ف

CHAPTER 1

INTRODUCTION

1.1 Background

The increasing demand for energy storage has become a global issue due to rising energy consumption, the finite supply of fossil fuels, and their environmental impact. As the world shifts toward sustainable energy solutions, electrochemical energy storage (EES) systems—such as batteries and electrochemical capacitors—play a crucial role in meeting the needs of various industries, including consumer electronics, transportation, aerospace, and stationary power systems. These storage technologies contribute to grid stability, lower fossil fuel dependence, and facilitate the transition to a more sustainable energy infrastructure [1-3]. Over the past years, lithium-ion batteries (LIBs) have dominated both the portable electronics market and the field of solid-state electrochemistry. However, concerns regarding the high cost and long-term availability of lithium have driven research into alternative technologies, such as sodium-ion batteries (SIBs), for large-scale energy storage applications [4]. Studies on LIBs and SIBs have primarily focused on the synthesis and advancement of high-performance anode and cathode materials to enhance energy density, cycling stability, and charge-discharge efficiency. Two-dimensional (2D) nanomaterials, including graphene and its composites, have been widely explored for their potential to improve battery performance by facilitating ion transport and providing a high surface area for enhanced ion adsorption and redox reactions [5].

Despite technological progress, LIBs still face challenges such as limited charge rate capacity, high production costs, low energy density, and reduced cycling stability. To address these limitations, researchers are actively developing new materials, particularly

2D nanomaterials, to enhance energy storage technologies [6]. Studies suggest that incorporating 2D materials significantly boosts the efficiency of lithium-ion batteries due to their superior mechanical strength, large surface area, and tunable electrical properties. Graphene, for instance, exhibits excellent stability and specific capacity, making it a promising material for high-performance LIBs [7]. The integration of 2D materials into battery electrodes allows for reversible ion insertion and extraction, thereby improving battery lifespan and efficiency [8].

Liquid-phase exfoliation, a widely used method for synthesizing 2D materials, facilitates the production of ultrathin structures that optimize electron transport and Li^+ ion movement in lithium-ion batteries. In essence, 2D materials offer great potential for enhancing energy density, charge-discharge rates, and long-term stability in lithium-ion battery technology [9].

Beyond graphene-based materials, boron nitride (BN) and boron carbon nitride (BCN) are emerging as potential alternatives for sodium-ion battery anodes. BN is known for its exceptional chemical and thermal stability, making it a promising candidate for improving SIB performance [10]. Research indicates that nitrogen-doped BN exhibits superior electrical properties, further enhancing its potential as an anode material [11].

Phagraphene, a nanosheet-like material, has demonstrated improved electrochemical performance, with its nitrogen-doped version exhibiting higher cell voltage compared to boron-doped or undoped variants [12]. Similarly, boron carbon nitride (BCN), a composite of boron, carbon, and nitrogen, has gained attention for its promising applications in energy storage. Its unique structure enhances electrical conductivity and stability, both of which

are critical for battery performance and longevity [13]. Studies suggest that BCN can significantly improve electrochemical efficiency by enabling more effective ion transport and storage, thereby advancing battery technology [14].

Fullerene-like materials, particularly fullerene derivatives, have also garnered significant interest for their potential use in rechargeable batteries due to their unique properties. These derivatives can be chemically modified with various functional groups to enhance their physicochemical characteristics, thereby optimizing their performance in energy storage applications. Their distinctive cage-like π -conjugated structure contributes to high electron mobility and structural stability, making them well-suited for use in advanced battery technologies [15].

Fullerene-like boron nitride nanocage have garnered significant interest. $B_{12}N_{12}$ is recognized as the smallest nanocage consisting of tetragonal BN rings interspersed with hexagonal BN rings, has received considerable attention [15]. However, the limited low electrical conductivity of the material can lead to poor performance rate and limited power density. The functionalization of these materials is essential as it enhances structural stability and augments the storage capacity and diffusivity of cations, rendering them appropriate for both anodes and cathodes [16]. Two-dimensional boron nitride, boron carbon nitride, and fullerene-like boron nitride nanocage ($B_{12}N_{12}$) are being considered promising materials for the improvement of the performance of ion batteries. Modifications involving doping have shown the ability to improve efficiency as anodic metal-ion battery materials.

Conducting polymers, a category of conjugated polymers exhibiting conductivity comparable to that of metals, have garnered significant interest for their potential in various technological applications, including energy storage, information processing, solar energy harvesting, and sensor technology [17]. These polymers have demonstrated effectiveness in enhancing metal-ion batteries by improving electrode conductivity, reinforcing the solid electrolyte interface (SEI) layer, and addressing challenges such as dendrite formation and low coulombic efficiency [18].

Their adaptability enables their utilization in multiple roles, such as anodic coatings, sulfur hosts, additives, and modifications to battery separators, all of which contribute to enhancing the efficiency of metal-ion batteries [19]. As a result, incorporating conducting polymers into 2D BN and BCN nanosheets is expected to boost electrical conductivity, facilitate charge carrier movement, and enhance ion transport efficiency.

Furthermore, the presence of substituent groups plays a crucial role in determining a material's electrical and conductive characteristics. These groups influence electronic structures at both the molecular and solid-state levels, directly impacting charge transport mechanisms [20]. Factors such as molecular geometry, packing configurations, and intermolecular interactions are integral to charge transfer processes. A thorough understanding of these molecular properties is essential for selecting and designing materials that can optimize the performance of semiconductor devices [21]. In addition, the incorporation of electron-donor substituent groups or electron-acceptor substituent groups into an optimum core structure allows the creation of p-type (hole transportation) and n-type (electron transportation) semiconductors, respectively [22]. This method

enables property optimization through strategic substitutions, which is essential for the optimization of the optoelectronic functionalities of the materials. Charge transportation in organic semiconductors typically occurs via a hopping mechanism, with the charge carriers hopping between local states [23]. According to the vision of Marcus' theory [24], substituents could modify the hopping rate, thereby increasing conductivity. Functionalization of boron nitride nanosheets, boron carbon nitride nanosheets, and boron nitride nanocages in this work aims to enhance their structural and electrical properties, leading to enhanced anodic performance in Li^+ , Na^+ , Be^{2+} , and Mg^{2+} ion batteries.

1.2 Problem statement.

The rising demand for renewable power systems, the popularity of electric vehicles, the depletion of fossil fuel reserves, and the increasing environmental concerns have generated the need for highly efficient energy storage systems. Despite much progress, the absence of stable, high-capacity anode materials with good cyclability and interfacial stability remains a pressing need, and more work must be done.

Anodic material optimization must be achieved to enhance conductivity and cell voltage in metal-ion batteries; however, several critical issues persist. For one, the current anode materials suffer from low conductivity, which compromises battery performance and necessitates creative solutions. Further optimization in ion diffusion and electronic conductivity must be achieved to reduce internal resistance in the battery. Interfacial resistance at the anode-electrolyte interface remains a major issue, as it compromises cell voltage and efficiency. In order to address these issues, new materials and design concepts must be designed that enhance energy density, power density, cycle life, stability, and affordability in metal-ion batteries simultaneously.

1.3 Objective of the study

This study utilizes density functional theory (DFT) calculations to explore the potential of poly-p-phenylene (PPPh)-functionalized boron nitride (BN) and boron carbon nitride (BCN) two-dimensional (2D) nanosheets. Additionally, it examines $B_{12}N_{12}$ boron nitride nanocages functionalized with various conducting polymers, including polypyrrole (PP), polyacetylene (PA), polythiophene (PT), and poly-p-phenylene (PPPh), as prospective anode materials for metal-ion battery applications. The specific objectives of this research are:

- **Model development:** Develop accurate computational models of BN and BCN 2D nanosheets functionalized with PPPh conducting polymers. Additionally, assess the impact of electron-donating and electron-withdrawing substituents on the electronic properties of PPPh.
- **$B_{12}N_{12}$ Nanocage Functionalization:** Develop models of $B_{12}N_{12}$ nanocages functionalized with PP, PA, PT, and PPPh conducting polymers.
- **Interaction and Adsorption Analysis:** Establish detailed interaction profiles and adsorption mechanisms for the functionalized 2D nanosheets and $B_{12}N_{12}$ nanocages.
- **Anodic Performance Evaluation:** Assess the predicted anodic performance of the modeled structures by examining key physicochemical properties, including ion mobility, diffusion dynamics, thermodynamic stability, work function, specific capacity, and open circuit voltage (OCV) for metal ions such as Li^+ , Na^+ , Be^{2+} , and Mg^{2+} .
- **Identification of Key Properties:** Determine the critical structural and chemical descriptors that govern the trends in the targeted material properties.

1.4 Some key scientific problems to be solved

This research aims to address key scientific challenges through Density Functional Theory (DFT) simulations, providing experimentalists with fundamental insights into the behavior

of BCN and BN nanosheets doped with PPPh conducting polymers, as well as $B_{12}N_{12}$ nanocages functionalized with PT, PP, PA, and PPPh conducting polymers. The ultimate goal is to guide the development of high-performance anodic materials for metal-ion batteries.

The study will focus on the following areas:

- **Electronic Structure and Conductivity:** Analyze how functionalization influences the electronic properties and conductivity of both the nanosheet and nanocage, as well as its impact on charge transport.
- **Stability and Reactivity:** Assess the stability of the functionalized polymer and its interaction with metal ions.
- **Metal Ion Adsorption and Diffusion:** Examine how metal ions (Li^+ , Na^+ , Be^{2+} , and Mg^{2+}) are adsorbed and diffused on the functionalized surfaces of nanosheets and nanocages, including the associated energy barriers.
- **Voltage Profile and Specific Capacity:** Calculate the voltage profile and specific capacity of the anode material, while investigating the mechanisms that influence its performance.

1.5 Scheme of Research Findings Report.

For ease of reading and comprehension, this thesis report is divided into five distinct chapters, as outlined below:

Chapter 1: Describe the urgent need to address energy storage systems, the unique properties of BNNS and BCNN 2D materials and $B_{12}N_{12}$ nanocage, the properties of conducting polymers and the possible impact of functionalization. A discussion of the problem statement, objective of the study and key scientific problems to be solved

follows.

Chapter 2: Provide an overview of the current literature on current 2D materials and nanocages for metal ion batteries.

Chapter 3: Theoretical insights on the design of high-performance metal-ion batteries: the role of conductive polymer functionalized boron nitride

Chapter 4: Functionalization of Boron Carbon Nitride Nanosheets with Conducting Polymers: A Strategy to Balance Conductivity and Electrochemical Performance in Metal Ion Batteries.

Chapter 5: Engineering anodic materials for metal-ion batteries with conducting polymer functionalized boron nitride nanocages: a DFT perspective.

Chapter 6: A summary of the study's findings is presented.

CHAPTER 2

LITERATURE REVIEW

2.1. Metal ion batteries as energy storage systems.

The necessity for energy storage has intensified due to the limited availability of fossil fuels and escalating apprehensions in environmental deterioration. Efficient energy storage systems are crucial for regulating the demand for clean and sustainable energy, especially as the globe shifts towards renewable energy sources. Secondary batteries, including metal ion batteries, are essential in this setting owing to their versatility, high energy conversion efficiency, and affordability [25]. Metal ion batteries, such as lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), and magnesium-ion batteries (MIBs), are significant contenders for energy storage applications. Nonetheless, each battery type possesses distinct restrictions. SIBs have difficulties associated with dendritic proliferation on the metal anode, whereas MIBs contend with an absence of appropriate cathode materials and limited electrochemical windows of the electrolyte [26]. In order to overcome the limitations of these metal ion batteries it is essential to understand their mechanism and working principles.

The mechanism of a metal ion battery involves the movement of metal ions (such as Li^+ , Na^+ , Mg^{2+} or Be^{2+}) during the charge and discharge processes **Fig 2.1**. While charging, metal ions are removed from the cathode material, pass through the electrolyte, and enter the anode material [28]. Conversely, during discharge, the ions move back to the cathode, generating electrical energy. This process is crucial for the battery's operation and efficiency, and understanding the ion conduction

phenomenon is essential for optimizing battery performance and achieving technological breakthroughs in metal ion batteries [29].

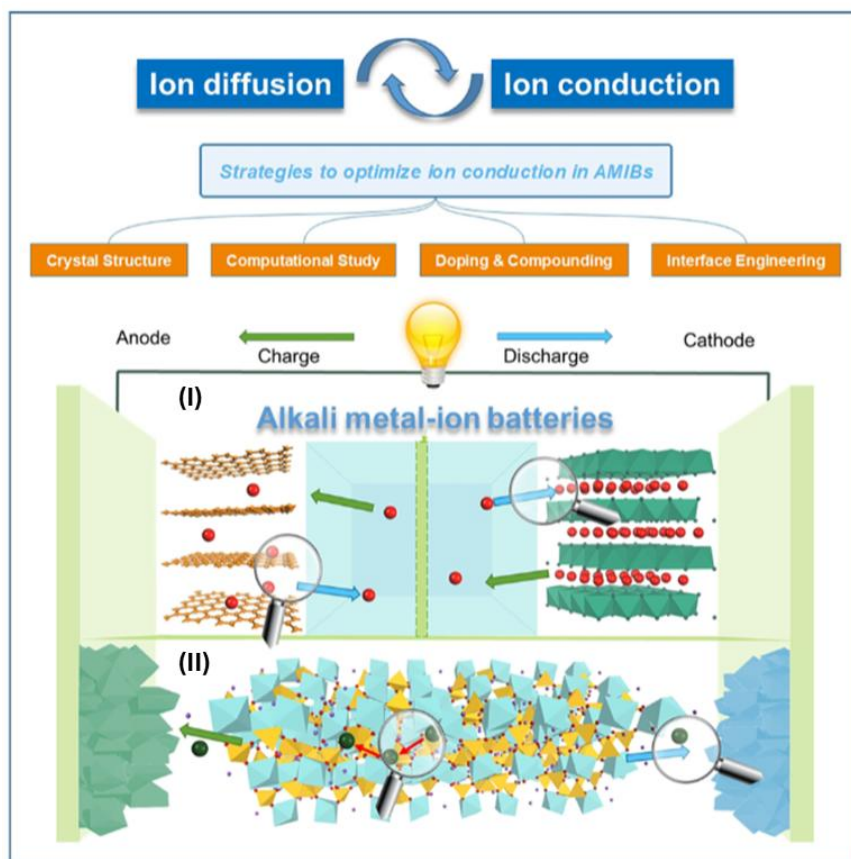


Figure 2.1 Schematic diagram of metal ion battery mechanism, (I) conventional and (II) All solid-state batteries [29]

2.2 2-dimensional materials in metal ion batteries.

Two-dimensional materials are vital in metal-ion batteries because of their properties and potential to greatly increase battery performance. They have large surface areas that offer more sites for the adsorption of metal ions and hence better storage capacities [30]. 2D materials also encourage fast diffusion of ions and hence fast charging and discharging rates. They are capable of conforming to volume changes during deintercalation and intercalation of ions hence increasing the cycle life of the batteries [31]. They also have high electrical conductivity, reducing internal resistance and increasing power density.

Their properties are easily modulated using chemical modifications, doping, and heterostructure formation, making it easier to fine-tune performance [32]. They are highly chemically and thermally stable, making them crucial for long-term reliability and safety. 2D materials possess high theoretical capacities for various metal-ion storage applications, making them versatile for different battery components, ultimately improving overall performance and lifespan. Additionally, they can be synthesized using scalable processes, making them highly suitable for commercial applications [33].

The characteristics of 2D materials render them advantageous for enhancing the efficiency, longevity, and adaptability of metal-ion batteries, essential for applications including portable devices, electric cars, and large-scale energy storage systems. Some popular 2D materials explored for metal ion batteries are discussed below.

2.2.1 Graphene

Graphene, as a 2D material, has been recognized as a promising candidate for metal-ion batteries due to its higher theoretical capacity compared to traditional graphite and its excellent electrical conductivity, which enhances charge and discharge rates [34]. Additionally, graphene improves the structural stability of the anode during charge-discharge cycles, ensuring long-term battery performance [35].

However, there are notable challenges in utilizing graphene for metal-ion batteries. One major limitation is that the adsorption energy of lithium ions on defect-free single-layer graphene is positive, which can hinder efficient ion storage and lead to lithium-ion cluster aggregation rather than uniform distribution [36]. Moreover, producing high-quality graphene is both expensive and difficult to scale up, limiting its commercial viability [37]. Ultimately, although theoretical studies offer significant insights, the intricate and time-intensive process of experimental validation can hinder the comprehensive study of graphene's potential in battery applications.

2.2.2 Borophene

Two-dimensional (2D) borophene, composed of boron atoms, has attracted significant interest for its potential use in metal-ion batteries due to its exceptionally high theoretical lithium storage capacity, surpassing that of conventional anode materials like graphite. Additionally, borophene has minimal diffusion energy barriers for alkali metal ions, allowing for rapid ion movement during charge and discharge cycles, which is essential for enhancing battery performance [38]. Its various structural polymorphs enable the fine-

tuning of its electrochemical properties, making it an even more attractive anode material [39].

However, there are considerable challenges in applying borophene to metal-ion batteries. The synthesis of high-quality borophene remains difficult, and scalable production methods have yet to be fully developed, potentially limiting its commercial viability [40]. Furthermore, its stability under real-world operating conditions—such as cycling and exposure to electrolytes—requires further investigation, as degradation could impact battery reliability and lifespan [41-42]. Ultimately, while theoretical research highlights borophene's promise, experimental validation of its effectiveness in practical battery applications is still lacking, necessitating further in-depth studies.

2.2.3 Silicene

Silicene, a 2D material composed of silicon atoms, has gained significant attention for its potential use in metal-ion batteries due to its high theoretical lithium storage capacity. It exhibits excellent electrical conductivity, enhancing the charge and discharge rates of batteries, making it a strong candidate for high-performance applications [43-44]. Additionally, its mechanical flexibility allows it to adapt to volume changes during lithium-ion insertion and extraction, which can improve the cycle stability of the anode material [45].

However, there are several challenges to using silicene in metal-ion batteries. One major limitation is the difficulty in synthesizing high-quality silicene, as scalable production methods are still under development, which may hinder its commercial application [46]. Another concern is its stability under real-world operating conditions—exposure to

electrolytes and continuous cycling can cause degradation over time, potentially affecting battery reliability and lifespan [47]. Furthermore, there is currently limited experimental evidence on silicene's actual performance in practical battery applications, emphasizing the need for more extensive research to validate its feasibility.

2.2.4 Phosphorene

Phosphorene has been explored as an anode material in lithium-ion and sodium-ion batteries due to its advantageous properties. Its high capacity and conductivity can lead to batteries with improved energy density and faster charging times [48]. Additionally, its flexibility and stability under cycling conditions make it a promising candidate for next-generation battery technologies. Phosphorene, while been a promising anode material for metal-ion batteries, faces several limitations that impact its performance. One significant challenge is its high sensitivity to air, moisture, and oxygen, which can lead to structural degradation and reduced performance over time [49]. Furthermore, although phosphorene can accommodate volume changes during lithium-ion insertion and extraction, it suffers from limited cycling stability, as repeated charge and discharge cycles can result in structural degradation and capacity loss [50]. The synthesis of high-quality phosphorene also presents difficulties, as current production methods may not yield the uniformity and quality necessary for commercial applications [51]. Furthermore, the presence of defects in the phosphorene can adversely affect its electronic properties and ion diffusion pathways; while some defects may enhance ion transport, excessive defects can lead to decreased conductivity and capacity.

2.3 Transition metal Dichalcogenides (TMD)

Transition metal dichalcogenides (TMDCs) have been widely studied as electrode materials for metal-ion batteries due to their unique properties and working mechanisms [52]. These materials function through intercalation, conversion, and pseudocapacitive processes, all of which are influenced by their layered structure, defects, and surface chemistry, ultimately impacting their electrochemical performance and storage capacity [53]. Some of the most commonly used TMDCs in metal-ion batteries include molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), titanium disulfide (TiS_2), tin disulfide (SnS_2), and molybdenum diselenide (MoSe_2).

MoS_2 , despite its high storage capacity, faces challenges related to structural degradation during cycling, which leads to capacity fading and relatively low electrical conductivity, limiting its rate performance [54-55]. Similarly, WS_2 struggles with structural integrity, cycling stability, and performance deterioration due to defects that hinder ion diffusion [56]. TiS_2 has a high theoretical capacity but suffers from poor cycling stability and low electronic conductivity, restricting its practical applications [57]. SnS_2 experiences significant volume fluctuations during ion insertion and extraction, causing mechanical degradation, while structural defects can lead to inconsistent electrochemical performance [58]. Lastly, MoSe_2 faces stability issues and the formation of undesirable phases during cycling, negatively affecting its overall capacity and efficiency [59].

Overall, while TMDCs show great promise as materials for metal-ion batteries, challenges related to structural integrity, conductivity, and stability must be addressed to optimize their performance in real-world applications.

2.4 MXenes

MXenes are a class of two-dimensional materials that have attracted significant interest for their potential use in metal-ion batteries due to their unique properties. They exhibit high electrical conductivity, which enhances charge transfer efficiency during battery operation, and their large surface area promotes ion adsorption, increasing both capacity and rate performance [60-61]. The layered structure of MXenes allows for easy intercalation of metal ions, improving cycling stability and capacity retention [62]. Some well-known MXenes explored for metal-ion batteries include Ti_3C_2 (Titanium Carbide MXene), Nb_2C (Niobium Carbide MXene), V_2C (Vanadium Carbide MXene), and Mo_2C (Molybdenum Carbide MXene). Their mechanical flexibility also helps them accommodate volume expansion during ion insertion and extraction, reducing structural degradation over repeated cycles [63]. Additionally, MXenes can be customized through surface functionalization to optimize their electrochemical performance by modifying their surface chemistry [64].

Despite their promising applications in metal-ion batteries, MXenes also have some limitations that can affect their performance. One major issue is their stability—MXenes tend to degrade when exposed to moisture and air, forming metal oxide structures. To prevent this, surface functionalization is often required, but these modifications can reduce storage capacity and overall electrochemical performance [65]. Defects and imperfections, such as vacancies, can also negatively impact their anodic performance by increasing energy barriers, which hinder efficient ion transport during battery operation [66]. Furthermore, their high metal-to-carbon ratio poses challenges, particularly in sodium-ion

batteries, where repulsive interactions between metal and sodium ions may reduce ion adsorption efficiency [67].

Additionally, while many potential MXene compositions exist, only a limited number have been thoroughly studied for metal-ion battery applications, restricting the understanding of their full potential and the development of optimized materials [68]. Lastly, the electrochemical performance of MXenes can vary significantly depending on their synthesis methods and surface terminations, making it difficult to achieve consistent results and scale up MXene-based battery technologies [69].

In conclusion, addressing challenges related to stability, structural defects, composition, and performance variability is crucial for unlocking the full potential of MXenes in energy storage applications.

2.5 Metals nitrides and electrides

Metal nitrides, such as titanium nitride (TiN) and vanadium nitride (VN), exhibit excellent conductivity and mechanical stability, making them suitable for lithium-ion and sodium-ion batteries [70], while electrides, including materials like Ca_2N and Y_2C , possess trapped electrons that enhance conductivity and electrochemical performance [71], although their application in lithium-ion batteries is limited due to adsorption challenges that can be mitigated through structural modifications like doping with elements such as oxygen or fluorine. Metal nitrides, while offering excellent conductivity and mechanical stability for lithium-ion and sodium-ion batteries, often face challenges related to structural integrity and defects that can hinder ion transport [72], whereas electrodes, despite their high

electron density enhancing conductivity and electrochemical performance, encounter limitations in practical applications due to adsorption challenges and the need for structural modifications, such as doping with elements like oxygen or fluorine to improve their performance in metal-ion batteries [73].

2.6 Boron nitride nanosheet (BNNS)

Hexagonal boron nitride (h-BN) nanosheets are a type of two-dimensional (2D) material that have gained considerable interest due to their exceptional properties and diverse applications. Structurally, they share similarities with graphene, as they consist of a honeycomb lattice formed by alternating boron (B) and nitrogen (N) atoms [74]. Figure 2.2 presents the chemical synthesis process of h-BN nanosheets. The bond length between B and N atoms is approximately 1.45 Å, while the interlayer spacing between adjacent h-BN layers varies between 3.3 and 3.41 Å. Because of their structural likeness to graphene, h-BN is commonly referred to as "white graphene" [75-76].

Electronically, h-BN is an electrical insulator with a wide bandgap of about 5.7 eV, though this can be modified to exhibit semiconducting behavior by introducing dopants or making structural adjustments [77]. These nanosheets also possess excellent thermal conductivity and stability, making them suitable for high-temperature applications. Additionally, they exhibit remarkable mechanical strength and flexibility, much like graphene [78]. Their chemical properties include being highly inert and resistant to oxidation, ensuring stability in various environments. Due to their high surface area, h-BN nanosheets are ideal for

applications in catalysis and adsorption. They also exhibit ultraviolet (UV) photoluminescence, showing promise for UV lasing and near-ultraviolet (NUV) detectors.

There are several methods for synthesizing h-BN nanosheets [79]. Liquid phase exfoliation involves dispersing bulk h-BN powder in a solvent like dimethylformamide (DMF) and using sonication to separate the nanosheets. The mixture is then stirred, sonicated for a few hours, centrifuged, washed with ethanol and deionized water, and finally dried [80]. Chemical vapor deposition (CVD) is another widely used method, where boron- and nitrogen-containing precursors are decomposed at high temperatures on a substrate to form h-BN layers. Other synthesis techniques include thermal decomposition, solvothermal synthesis, and microwave-assisted exfoliation, each with distinct advantages and limitations.

h-BN nanosheets have a diverse range of applications. They hold promises for environmental remediation, particularly when doped with transition metals, serving as nanocatalysts for wastewater treatment and dye degradation. Additionally, doped h-BN nanosheets exhibit antimicrobial properties, making them valuable in antimicrobial applications. Their high surface area and sensitivity also make them suitable for various sensing applications. Moreover, their porous structure enhances their potential for hydrogen storage [81].

Hexagonal boron nitride (h-BN) is also a promising candidate for enhancing the performance of metal-ion batteries (MIBs), including lithium-ion (Li-ion), sodium-ion (Na-ion), and magnesium-ion (Mg-ion) batteries [82]. Its high thermal conductivity, mechanical strength, and chemical stability make it an excellent material for improving

electrode performance [83]. h-BN can be used in both anodes and cathodes, where its large surface area provides more sites for ion intercalation, enhancing capacity and cycle life. Its superior thermal conductivity and mechanical strength also improve structural stability during cycling, minimizing capacity fading. Additionally, h-BN enhances charge and discharge efficiency by improving ionic conductivity, which leads to better energy efficiency and reduced energy loss. Furthermore, its chemical inertness helps stabilize the electrolyte, preventing unwanted reactions with electrode materials and enhancing battery safety [83].

However, there are some challenges associated with using h-BN in metal-ion batteries. Despite its excellent thermal conductivity, h-BN has poor electrical conductivity, which limits its ability to efficiently transport charge. To address this issue, it is often combined with conductive materials like graphene or carbon nanotubes. However, this approach increases production complexity and costs [84]. Additionally, these modifications require expensive and specialized equipment, making large-scale production challenging. Therefore, exploring alternative strategies to enhance the conductivity of h-BN nanosheets is necessary.

HEXAGONAL BORON NITRIDE SYSTEM

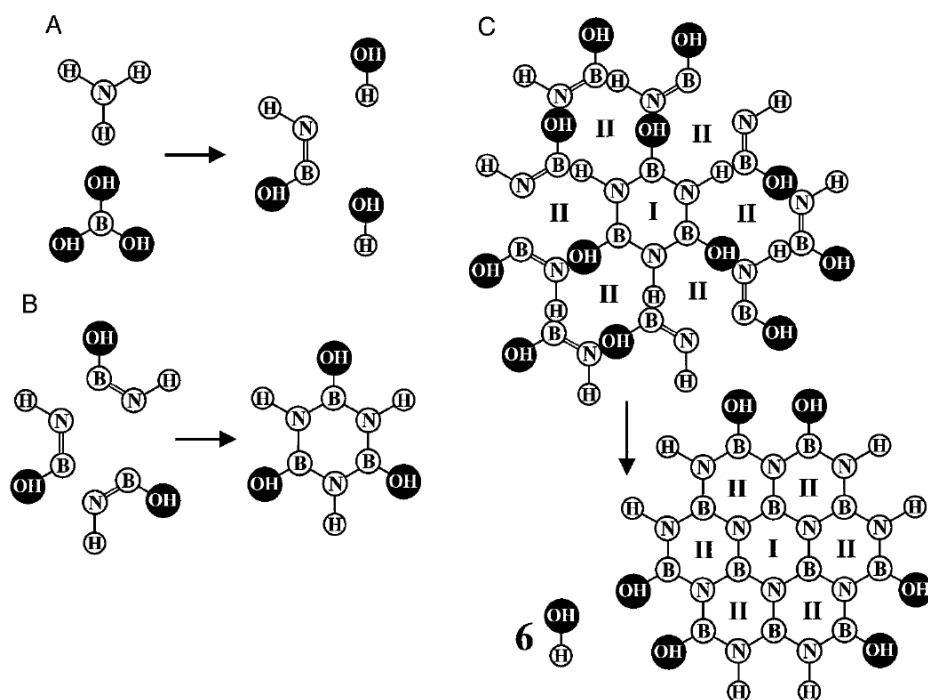


Figure 2.2 Schematic Process showing the formation of hexagonal boron nitride.[85]

2.7 Boron carbon nitride nanosheet (BCNNS)

Two-dimensional (2D) materials known as Boron Carbon Nitride (BCN) nanosheets are hybrid materials that have the properties of graphene and boron nitride (BN) combined. They consist of boron (B), carbon (C), and nitrogen (N) atoms in a hexagonal lattice structure [86]. Owing to their tunable mechanical, electronic, and thermal properties, BCN nanosheets have gained considerable attention for various applications [87]. They are structurally a combination of graphene and the hexagonal structure of BN. The arrangement of the B, C, and N atoms may differ from one another, thus forming different stoichiometries such as $B_2C_2N_2$, B_2C_3N , and BN_2C_3 . This renders the material with properties that range from graphene-like conductivity to h-BN-like insulation depending on composition and atomic structure [88].

BCN nanosheets exhibit highly tunable electronics with their bandgap being modifiable from 0 eV (metal) to approximately 5 eV (insulator) [89]. They are hence appropriate for semiconductor uses in electronic and optoelectronic devices. Mechanically, BCN nanosheets are strong and ductile with high tensile strength and mechanical stress resistance like graphene and h-BN [90]. They are also good heat conductors and hence appropriate for heat management applications and are thermally stable at high temperatures, making them suitable for high-temperature conditions. Chemically, BCN nanosheets are oxidation-resistant and chemically inert with good corrosion resistance. They also exhibit high specific surface area, making them ideal for catalysis and adsorption [91].

Optically, BCN nanosheets exhibit structure- and composition-dependent tunable photoluminescence and are thus promising candidates for photodetectors and light-emitting devices [92]. There are different synthesis pathways for BCN nanosheets, each with its own merits and demerits. Chemical Vapor Deposition (CVD) is one of the most widely used methods, where boron-, carbon-, and nitrogen-containing precursors are decomposed at high temperatures on a substrate. CVD yields high-quality, large-area nanosheets with controlled composition but requires specialized equipment and high temperatures [93]. Thermal decomposition is another method where chemicals like boric acid, urea, and melamine are decomposed at high temperatures to yield BCN nanosheets. It is cost-effective and scalable but poses the risk of incorporating impurities [94-95].

BCN nanosheets can be used as cathode and anode materials in metal-ion batteries. They are electronically tunable to allow for bandgap modifications to facilitate ion transport and electrochemical activity [96]. Their high surface area and composition tunability provide more sites for metal-ion intercalation, which can increase battery capacity and charge/discharge efficiency [97]. Furthermore, their chemical inertness and oxidation resistance can stabilize the electrolyte in metal-ion batteries, reducing undesirable reactions with electrode materials and enhancing the overall safety and performance of the battery.

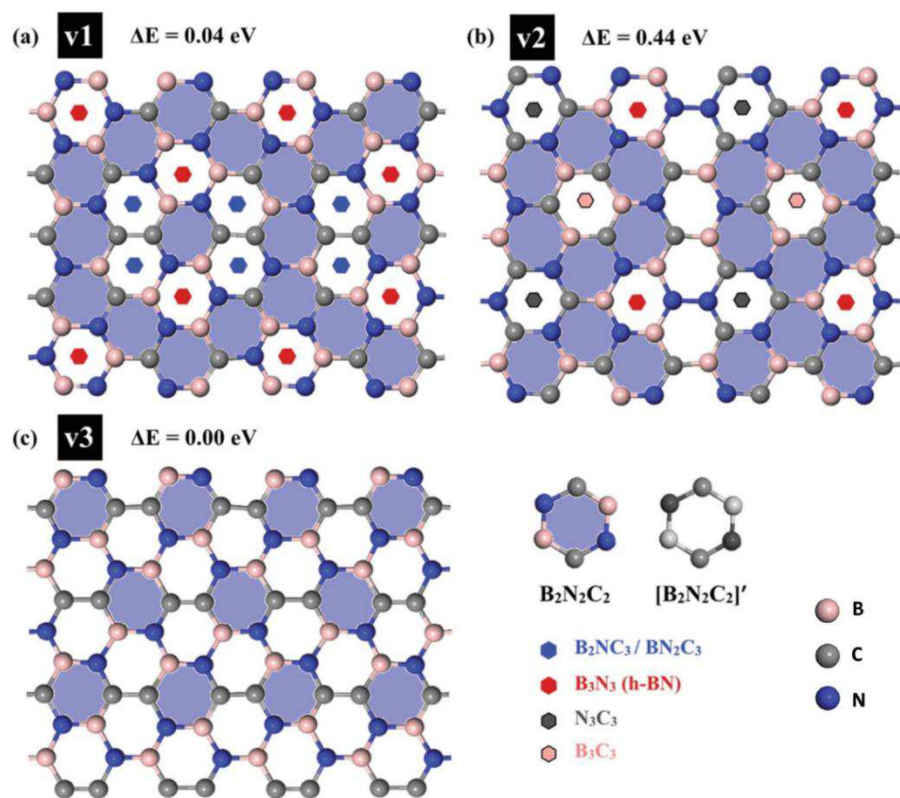


Figure 2.3 Schematic diagram showing three possible h-BCN monolayer structures, namely (a) h-BCN_v1, (b) h-BCN_v2, and (c) h-BCN_v3 with relative stability.[98]

2.8 Boron nitride nanocage

Boron Nitride (BN) nanocages are nanostructures composed of boron (B) and nitrogen (N) atoms arranged in a cage-like geometry [99]. They are comparable to carbon fullerenes such as C_{60} but consist of alternating N and B atoms. Due to their nanoscale nature and the intrinsic properties of boron nitride, BN nanocages exhibit unique properties [100]. Structurally, they have a hollow, cage-like form with alternating N and B atoms arranged in a hexagonal lattice, similar to hexagonal boron nitride (h-BN). The most common BN nanocages include $B_{12}N_{12}$, $B_{24}N_{24}$, and $B_{32}N_{32}$ (**Figure 2.4**). The bond length between N and B atoms in BN nanocages is approximately 1.45 Å, similar to that of h-BN.

Electronically, BN nanocages are wide-bandgap semiconductors with a bandgap of around 5-6 eV, similar to bulk h-BN. Their electronic properties can be modified through doping, functionalization, or structural adjustments to the size and shape of the nanocage [101]. Mechanically, BN nanocages are highly robust, exhibiting excellent strength and stiffness, much like other boron nitride nanostructures [102]. They are also lightweight, making them particularly useful for nanocomposites and lightweight materials.

There are various synthesis methods for BN nanocages, each with its advantages and disadvantages. One commonly used method is the arc discharge technique, in which an electric arc is generated between electrodes made of boron- and nitrogen-containing materials in an inert gas atmosphere such as argon or nitrogen [103]. The high temperature from the arc discharge vaporizes the electrodes, and the resulting vapor condenses to form BN nanocages. This method is cost-effective and straightforward but offers limited control over the nanocage size and shape and may introduce impurities.

BN nanocages have a wide range of applications in different fields. In drug delivery, they act as nanocarriers due to their biocompatibility, large surface area, and ability to encapsulate drugs within their hollow structure. Their high surface area and tunable electronic properties also make them suitable for use in supercapacitors and battery electrodes for energy storage [104]. Additionally, their porous nature and high surface area increase the number of active sites available for metal-ion storage, improving battery capacity. The porosity of BN nanocages also facilitates efficient ion diffusion, leading to faster charge and discharge cycles, making them ideal for energy storage devices.

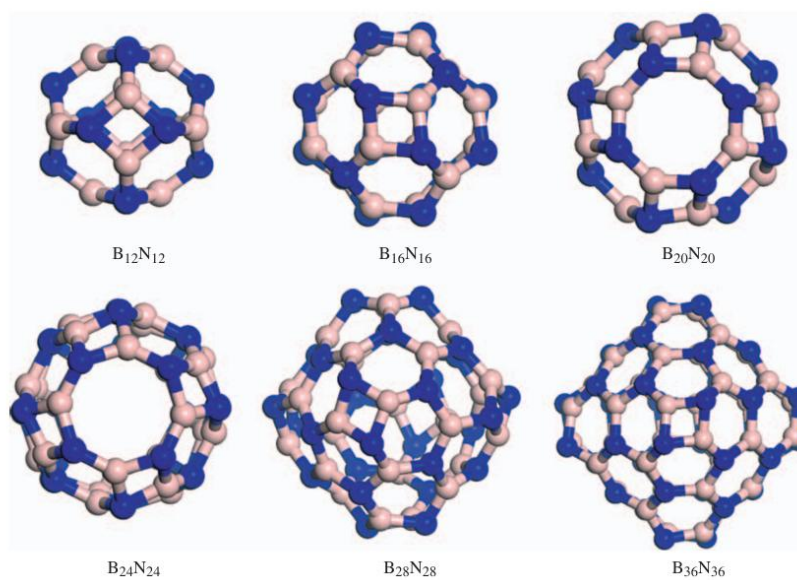


Figure 2.4 Structures of BN nanocages of high symmetry: $B_{12}N_{12}$ (Th), $B_{16}N_{16}$ (Td), $B_{20}N_{20}$ (C4h), $B_{24}N_{24}$ (S₈), $B_{28}N_{28}$ (T), $B_{36}N_{36}$ (T_d). [105]

2.9 Conducting polymers

Conducting polymers are a unique class of polymers that exhibit electrical conductivity, often comparable to metals. They are widely utilized in various applications, such as supercapacitors, sensors, and flexible electronics. The primary types of conducting polymers are included in **Figure 2.5**. [106]

- Polyacetylene (PA) exhibits a wide range of conductivity values, spanning from 10^{-5} to 10^3 S/cm, depending on the extent of its doping. Functionalizing polyacetylene involves introducing dopants such as electron acceptors (Nitro groups) or electron donors (e.g., Amino groups). This doping process generates charge carriers, including polarons and bipolarons, which enhance electron transport. When polyacetylene is used for functionalization, it improves the conductivity of semiconductors by forming conductive pathways and introducing additional charge carriers.
- polyaniline (PANI): The conductivity of polyaniline (PANI) varies from 10^{-10} to 10^2 S/cm depending on its doping level and oxidation state. When doped with acids such as HCl, the imine nitrogen atoms in PANI become protonated, generating polarons that enhance conductivity. In its emeraldine base form, PANI is non-conductive, but upon protonation, it transitions into a conductive state. Functionalizing a semiconductor with PANI improves conductivity by forming a conductive network and facilitating charge transfer at the interface.
- Polypyrrole (PP): Polypyrrole's conductivity spans from 10^{-2} to 10^2 S/cm, depending on the doping level and synthesis conditions. Doping with anions such as chloride (Cl^-) or nitrate (NO_3^-) during polymerization introduces positive charges along the polymer

backbone, enhancing conductivity. When a semiconductor is functionalized with polypyrrole, the conductivity increases due to the formation of conductive pathways and the introduction of charge carriers.

- Polythiophene (PT) and Poly(3,4-ethylenedioxythiophene) (PEDOT) exhibit conductivities ranging from 10^{-4} to 10^3 S/cm, depending on their molecular structure. Functionalizing a semiconductor with polythiophene or PEDOT enhances conductivity by forming a conductive network and facilitating charge transfer. These polymers can be doped with electron acceptors such as iron chloride (FeCl_3) or through electrochemical doping, introducing charge carriers that improve conductivity.
- Poly p-phenylene (PPPh) typically exhibits conductivity levels ranging from 10^{-8} to 10^{-2} S/cm, but this can be improved through functionalization. Doping PPPh with electron acceptors or donors generates charge carriers, enhancing its electrical properties. The doping process may also involve chemical modifications to the polymer backbone. Functionalizing a semiconductor with PPPh improves conductivity by introducing charge carriers and creating conductive pathways.

2.9.1 Mechanism of Functionalization and Conductivity Enhancement:

The conductivity of conducting polymers is largely due to the presence of conjugated π -electron systems along the polymer backbone [107]. Functionalization, usually through doping, introduces charge carriers such as polarons, bipolarons, or solitons into the polymer matrix, facilitating electron transport and enhancing conductivity [108].

When conducting polymers are used to functionalize semiconductors, they enhance the semiconductor's conductivity through several mechanisms:

1. Formation of Conductive Pathways: The conducting polymer creates a network of conductive pathways within the semiconductor, aiding electron transport.

2. **Introduction of Charge Carriers:** Doping introduces additional charge carriers that migrate into the semiconductor, boosting its conductivity.
3. **Interface Engineering:** The interface between the conducting polymer and the semiconductor can be engineered to minimize energy barriers, promoting efficient charge transfer.
4. **Morphological Control:** The morphology of the conducting polymer can be controlled to optimize its interaction with the semiconductor, further enhancing conductivity.

In summary, conducting polymers significantly improves semiconductor conductivity through doping, the formation of conductive pathways, and interface engineering [108]. The specific conductivity values and mechanisms depend on the type of conducting polymer and the characteristics of the semiconductor.

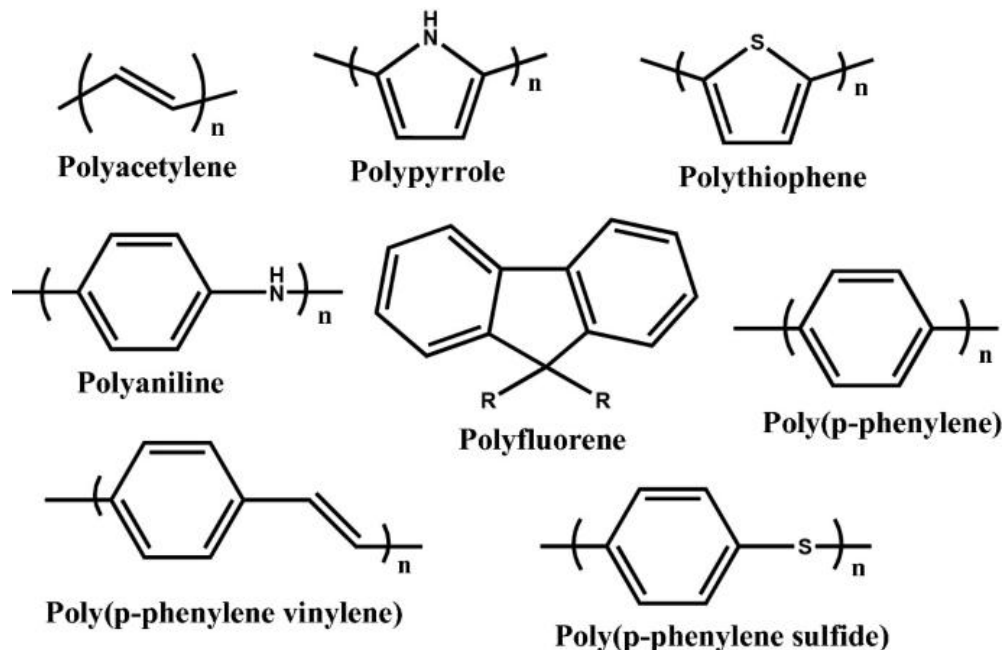


Figure 2.5 Main chain repeating units of common conducting polymers [106]

2.10 Density Functional Theory (DFT) Calculations Techniques.

Density Functional Theory (DFT) is a widely used computational tool to examine systems with more than a single electron like atoms, molecules, and solids. The quantum mechanical method computes electronic structure and material properties by solving the Schrödinger equation. Unlike traditional wave function-based approaches, DFT simplifies electron interactions with electron density as a primary variable. The simplification enables efficient prediction of significant material properties such as electronic band structure, total energy, atomic forces, and vibrational behavior. Due to efficiency and accuracy, DFT is crucial in metal-ion battery research, electrode material modeling, metal-ion diffusion calculations, electrochemical reaction studies, tuning of battery performance, and new material development.

CHAPTER 3

THEORETICAL INSIGHTS ON THE DESIGN OF HIGH-PERFORMANCE METAL-ION BATTERIES: THE ROLE OF CONDUCTIVE POLYMER FUNCTIONALIZED BORON NITRIDE

3.1 Introduction

The increasing global demand for energy, alongside the rapid depletion of fossil fuel reserves, environmental pollution, and health risks, has sparked a heightened interest in sustainable, clean, and abundant sources of energy, such as tidal, wind, and solar power. However, the inherent intermittency and variability of these renewable sources have accelerated the development of advanced energy storage systems to ensure a stable energy supply. Among these, rechargeable lithium-ion batteries (LIBs) stand out for their high efficiency as electrochemical storage devices and are widely used in portable electronics due to their broad voltage range and high energy density [111-114].

Despite their promise, lithium-ion batteries face several challenges, such as limited specific capacity, relatively high costs, diminishing mineral resources, and safety concerns [115-116]. Commercially established LIBs with graphite anodes, offering a modest capacity of only 372 mAh/g, continue to fall short of meeting the increasing demands for energy storage systems, especially in terms of rapid charge and discharge capabilities, hindered by graphite's high diffusion barrier [117]. Consequently, the search for new anode materials with high conductivity, enhanced capacity, and superior rate performance has become a key area of research.

Two-dimensional (2D) materials have demonstrated significant promise for enhancing performance in LIBs, particularly in terms of high-rate capability and impressive cycling

stability. Examples of some studied 2D materials for metal ion batteries (MIBs) include ordered graphene and reduced graphene oxide sheets [118-119], graphene-based composites [120-121], transition metal oxide sheets [122-123], transition metal dichalcogenide sheets [124], and MXene sheets [125-127]. Monolayered boron nitride nanosheets are acknowledged as very versatile two-dimensional materials due to their exceptional thermal and chemical stability [128]. The hexagonal BN nanosheet is a 2D material consisting of alternating boron and nitrogen atoms arranged in a honeycomb pattern with an equal number of boron and nitrogen atoms. [129-130]. It demonstrates remarkable thermal conductivity of 2000 W/mK, electrical insulation with a wide bandgap of 5.9 eV, and chemical stability, and can be synthesized via the chemical vapor deposition method [131-134]. Nonetheless, the distinctive characteristics of BNNS, especially their tunable bandgap, and stability, allow control over their electronic properties through thickness modification, strain engineering, functionalization, and defect introduction and could position them as a promising candidate for the development of metal ion-based batteries [135-137].

Recent studies on BN have employed various approaches to adjust its band gap, through chemical doping, and defect engineering. Similarly, band gap tunneling through hydrogenation, fluorination, graphene-BN heterostructures, BN nanoribbons, and transition metal doping have been explored [138-139]. Given the remarkable thermal stability, effective heat dissipation, and chemical inertness of BN materials, along with the considerable hazards associated with overheating in metal-ion batteries, utilizing the beneficial properties of BNNS for improved electrochemical storage systems could signify significant progress in the advancement of such systems, especially those designed to

function at high temperatures. Hence functionalization can be utilized to achieve this objective, thus, enhancing the electronic properties of BNNS materials [140], augmenting their stability [141], modifying their electronic bandgaps [142], and improving their performance in energy storage systems. Despite these findings, the functionalization of BNNS particularly with electron-withdrawing or donating groups on the functional molecule has not been explored. However, many reports, for example, Hussain et al. [143] Investigated the influence of Be doping on the band gap of hexagonal boron nitride nanosheets. The systems were examined by varying the dopant concentration from 3.125% to 12.5%, revealing that the electron-deficient impurity induces a downward shift in the Fermi level, resulting in a minimized band gap. Khan et al. [144] examined the borophene/boron nitride (B/BN) interface as an electrode for lithium-ion batteries (LIBs). The research demonstrated enhanced thermal and mechanical stability of the interface material, showcasing a specific charging capacity of 1698 mAh/g, which surpasses that of bare borophene and other two-dimensional materials. In a separate investigation, Hosseinian et al. [145] utilized density functional theory to examine the prospective application of phosphorus-doped with boron nitride nanosheets for sodium-ion batteries. The study concluded that substituting three nitrogen atoms in the hexagonal ring with larger phosphorus atoms markedly enhances the performance of the sheet, resulting in an approximate increase of 0.67 V in the initial cell voltage, accompanied by an extended discharge duration. The performance improvement of currently available ion batteries is limited by the ion storage capacity of anode materials. Therefore, a continuous effort is being made to create superior anode materials for high-performance lithium-ion batteries.

Herein, we employ first-principles calculations to explore the enhancement of electrical characteristics and anodic voltage performance of boron nitride nanosheets (BNNS) through functionalization with poly-*p*-phenylene (PPPh). The focus is on understanding the impact of functional groups namely hydroxyl, amino, methoxy, methyl, carboxyl, cyano, nitro, fluoro, chloro, and bromo on the PPPh conducting polymer and their role in improving BNNS anodic performance. Functional groups significantly influence a material's electrical properties by altering its molecular and solid-state electronic structures, thereby affecting charge transport [146]. In addition, incorporating electron-rich donors or electron-deficient acceptors into a suitable core structure can yield p-type (hole transport) or n-type (electron transport) semiconductors, respectively [147]. This functionalization is expected to work in synergy in the enhancement of the conductivity and anodic performance of Li^+ , Na^+ , Be^{2+} , and Mg^{2+} ion batteries. The present study lays the groundwork for advancing functionalized materials tailored for high-performance energy storage applications, offering insights into the design principles necessary to optimize BNNS-based systems for next-generation battery technologies.

3.2 Computational methods

All calculations were carried out with the DMol3 module of Material Studio software [148]. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA), which gives good predictions of electronic quantities and adsorption energies [149-152], was used to calculate electron exchange-correlation energy. The Grimme dispersion correction (DFT-D3) was employed to account for long-range van der Waals interactions [153-155]. A smearing value of 0.005 Ha was also utilized to calculate orbital occupancy.

The double numerical plus polarization (DNP) basis set was used to effectively describe valence electrons and to precisely calculate electrostatic interactions. For structure optimization and energy convergence with high precision, the following global cut-off values were used: 5.2 Å for structure optimization, 0.002 Å for displacement, 0.001 Ha/Å for maximum force, and 1.0×10^{-6} Ha for self-consistent field (SCF) calculations. For preventing artificial interactions between periodic layers, a large vacuum spacing of approximately 20 Å was used.

The adsorption energies of metal ions and atoms (M/M^{n+}) on pristine BN nanosheets (BNNS) and poly-p-phenylene-functionalized BNNS (BNNS-PPPh) were determined using the equation below:

$$E_{ad} = E_{complex} - [E_{sheet/PPPh-BNNS} + E_{(M/M^{n+})}] \quad (1)$$

Where E_{ad} , $E_{complex}$, $E_{sheet/PPPh-BNNS}$, and $E_{(M/M^{n+})}$ represents the adsorption energy, energy of the adsorbed metal atoms/ions on the BNNS or PPPh-BNNS, energy of the bare BNNS or PPPh-BNNS, and the energy of the isolated metal atoms/ions. Similarly, changes in HOMO-LUMO energy gap (ΔE_g) upon the adsorption of various metal atoms/ions on the bare BNNS and/or PPPh-BNNS were computed as a basis of effective interaction and adsorption sensitivity as depicted below:

$$\%E_g = \left[\frac{E_{g_{complex}} - E_{g_{sheet}}}{E_{g_{sheet}}} \right] \times 100\% \quad (2)$$

where E_g , $E_{g_{complex}}$ and $E_{g_{sheet}}$ represents the HOMO-LUMO energy gaps of bare BNNS or PPPh-BNNS, the energy gap of the complex, and the energy gap of the bare sheet after the metal atoms/ions ($E_{M/M^{n+}}$) have been adsorbed, respectively.

In addition, initial cell voltages (V_{cell}), was computed similarly to our previous work [140] using the Nernst equation below:

$$V_{cell} = \frac{-\Delta G_{cell}}{zF} \quad (3)$$

where V_{cell} , ΔG_{cell} , z , and F represents the initial cell voltage, Gibbs free energy, the charge on the metal ions (the electrolytic cations) and F is the Faraday's constant with the value of (96500 C/mol or 23.061 kcal/volt.mol). As depicted in Equation 4:

$$\Delta G_{cell} = \Delta E_{cell} + P\Delta V - T\Delta S \quad (4)$$

Since the entropy contribution and the effects of the volume are considered negligible (<0.01V) [140]. Hence, the Gibbs free energy (ΔG_{cell}) representing the energy of the overall cell reactions under investigation would be nearly equal to the internal energy change [156]. Where ΔE_{cell} denotes the change in the adsorption energy of the bare BNNS and/or PPPh-BNNS under investigation.

The work function (Φ) is an important parameter that can give insights into the minimum energy required to extract one electron from the Fermi level [157-158]. For conductors and semiconductors-based materials, (Φ) can estimate their potential as electrodes in electronic devices as well as solar cells [159-160]. Using the theoretical methods proposed by Wu et al. [159] the work function was estimated with the following equation.

$$\Phi = V_{el(+\infty)} - EF \quad (5)$$

$$EF = \left[\frac{E_{HOMO} - (E_{HOMO} - E_{LUMO})}{2} \right] \quad (6)$$

where E_{HOMO} , E_{LUMO} , EF , and $V_{el(+\infty)}$ denote the energies of the highest occupied molecular orbital, the energy of the lowest unoccupied molecular orbital, the energy of Fermi level, and the energy of the electron outside the surface of the metal/ion-BNNS or PPPh-BNNS systems. Since $V_{el(+\infty)} = 0$. Therefore, Φ was estimated as:

$$\Phi = -EF \quad (7)$$

Thermal stability refers to the temperature range within which a material remains intact without deformation, making it a crucial property for high-temperature applications. The thermal stability of the anodic material was evaluated using dynamics simulations at different temperatures on the DMol³ module.

3.3 Results and discussion

3.3.1 Structural optimization and electronic properties.

To investigate the anodic performance of BNNS and the impact of functionalization, hexagonal BNNS, poly-p-phenylene (PPPh), and selected electron-donating (EDG) and electron-withdrawing groups (EWG) - hydroxyl, amino, methoxy, methyl, carboxyl, cyano, nitro, fluoro, chloro, and bromo - were modelled and optimized (**Figure 3.1**). The BNNS unit cell, comprising one boron and one nitrogen atom, featured a lattice parameter of $a=b=2.56 \text{ \AA}$, consistent with previous data [161]. A (5×5) supercell, containing 50 atoms (25 boron and 25 nitrogen), was used for structural analysis. The EWG and EDG groups were attached to the meta positions of three repeat units of PPPh (**Figure 1d–m**), while the conductivity, charge carrier mobility, and anodic voltage in the functionalized BNNS system were estimated.

The formation energies of functionalized BNNS through PPPh attachment on boron and nitrogen atoms were determined. The average formation energies were -3.21 eV for boron and -2.59 eV for nitrogen, indicating greater stability when attached to boron. Consequently, the optimized structural geometries of various EWG and EDG groups on PPPh-functionalized sheets are displayed in **Figure 3.2**. Notably, these modifications

preserved the planarity of the BNNS sheet while enhancing its electronic properties, as illustrated in **Figure 3.3**.

The calculated average B-N bond distance in pristine BNNS is 1.45 Å, consistent with previously reported experimental [162] and theoretical [161] values, validating the computational methods employed in this study. Upon functionalization with PPPh, the B-N bond distance slightly increases to 1.46 Å. Further functionalization of PPPh with various electron-withdrawing (EWG) and electron-donating groups (EDG) results in bond distances ranging from 1.47 Å to 1.52 Å. The observed increase in bond distance with EWG-functionalized PPPh is attributed to the inductive effect, which withdraws electrons from the polymer backbone, reducing the electron density on the boron atom and weakening the B-N bond. Conversely, EDG-functionalized PPPh delocalizes electrons via resonance, increasing the partial negative charge on the PPPh carbon atoms. This enhanced electron interaction with the boron atom similarly weakens the B-N bond. For $M/M^{n+}@BNNS$ complexes, the B-N bond distances remain unchanged, except for $Be^{2+}@BNNS$, which shows a slight increase. This is likely due to the interaction between the vacant 2S orbital of Be and the electron density of BN's nitrogen atom, causing a distortion in the B-N bond (**Table 3.1**). These findings illustrate the significant influence of functional group modifications on the structural and electronic properties of PPPh-BNNS complexes.

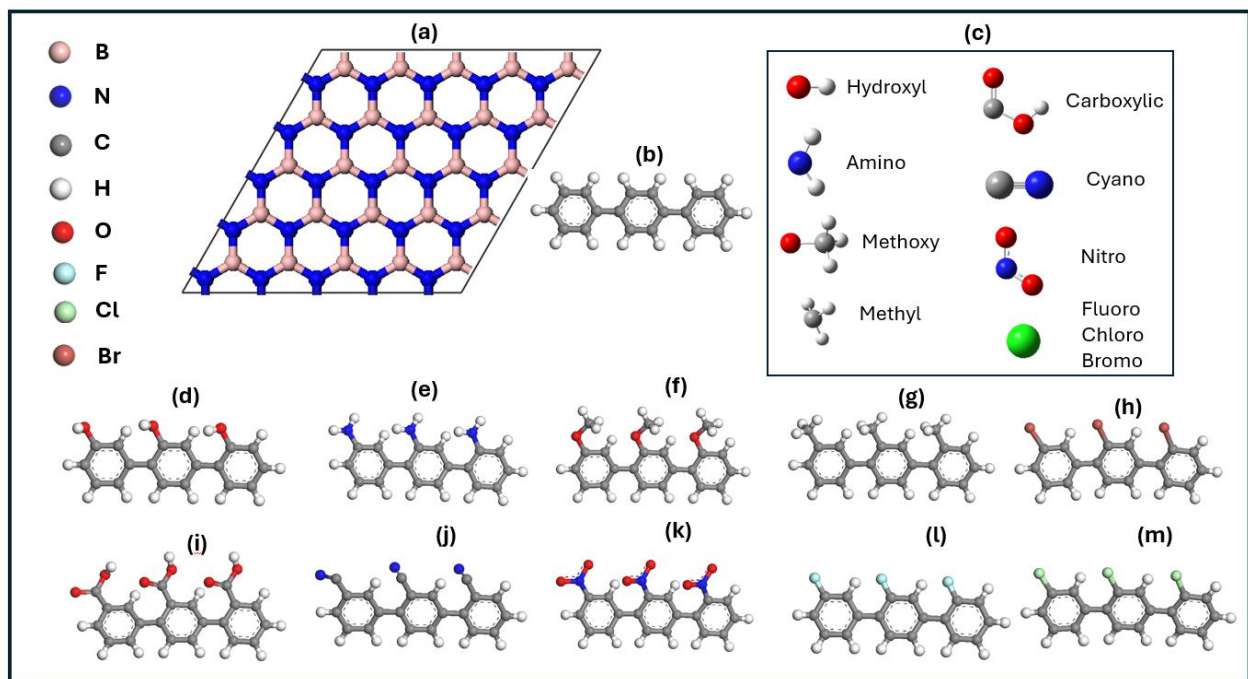


Figure 3.1 Optimized geometries of (a) pristine boron nitride nanosheet (BNNS), (b) repeat unit of the poly-p-phenylene (PPPh), (c) selected electron withdrawing and electron donating groups (EWG & EDG), (d) hydroxy@PPPh, (e) amino@PPPh, (f) methoxy@PPPh, (g) methy@PPPh, (h) bromo@PPPh, (i) carboxyl@PPPh, (j) cyano@PPPh, (k) nitro@PPPh, (l) fluoro@PPPh, and (m) chloro@PPPh.

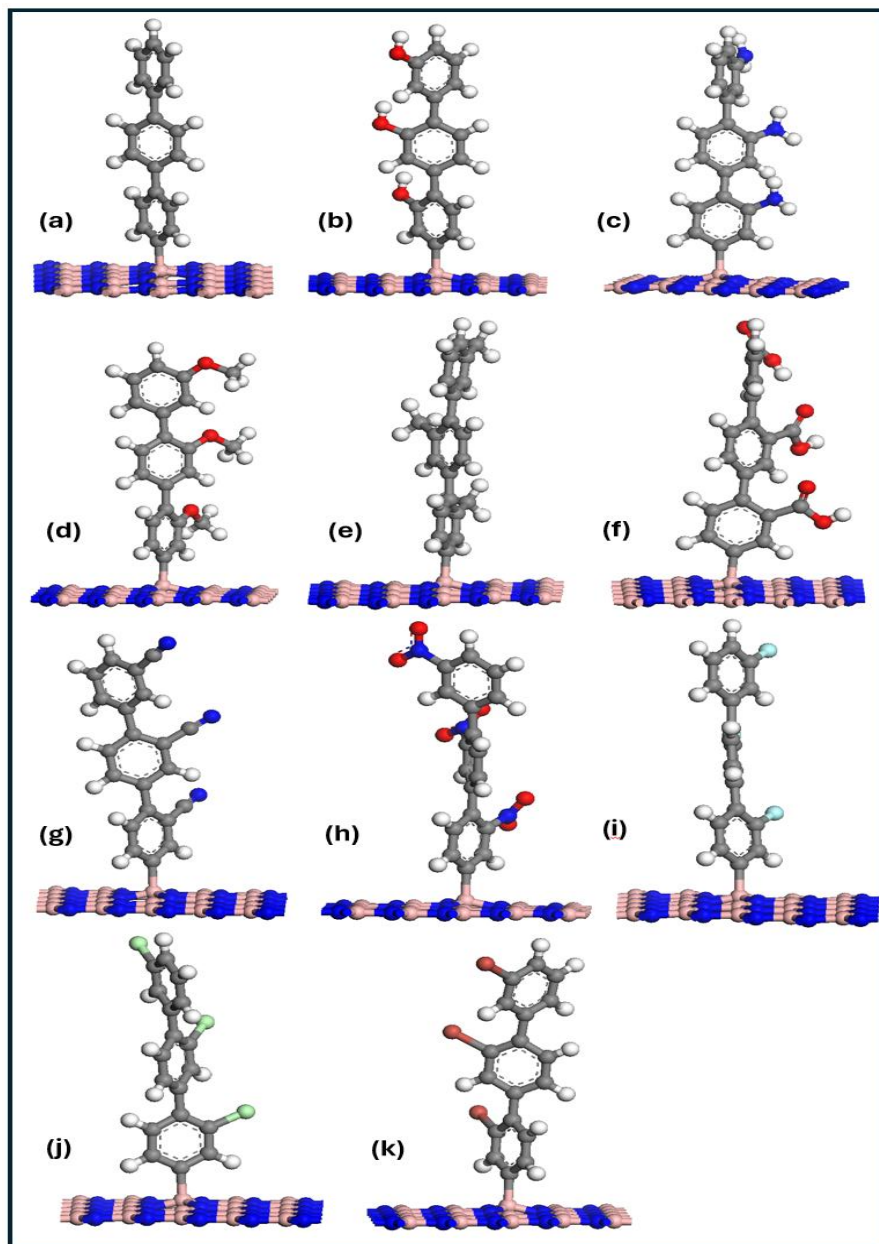


Figure 3.2 Optimized geometries of (a) PPPh-BNNS, (b) hydroxy@PPPh-BNNS, (c) amino@PPPh-BNNS, (d) methoxy@PPPh-BNNS, (e) methyl@PPPh-BNNS, (f) carboxyl@PPPh-BNNS, (g) cyano@PPPh-BNNS, (h) nitro@PPPh-BNNS, (i) fluoro@PPPh-BNNS, (j) chloro@PPPh-BNNS, (k) bromo@PPPh-BNNS

Table 3.1 Calculated boron to nitrogen bond distance in BNNS and adsorption distances of metal and metal-ion on bare BNNS and PPPh-BNNS complex

Complex	B-N bond distance (Å)	M-B bond distance (Å)	M-N bond distance (Å)
Li@BNNS	1.44	2.44	2.39
Li⁺@BNNS	1.43	2.37	2.26
Na@BNNS	1.45	2.99	3.00
Na⁺@BNNS	1.44	2.47	2.74
Be@BNNS	1.45	3.33	3.35
Be²⁺@BNNS	1.52	1.97	1.73
Mg@BNNS	1.45	3.51	3.66
Mg²⁺@BNNS	1.45	2.14	2.29
Li@PPPh-BNNS	1.47	2.35	2.10
Li⁺@PPPh-BNNS	1.48	2.32	2.15
Na@PPPh-BNNS	1.48	3.05	2.72
Na⁺@PPPh-BNNS	1.46	2.74	2.66
Be@PPPh-BNNS	1.47	2.86	2.90
Be²⁺@PPPh-BNNS	1.46	2.11	1.89
Mg@PPPh-BNNS	1.48	3.15	2.82
Mg²⁺@PPPh-BNNS	1.47	2.29	2.15

3.3.2 Impact of Functionalization on BNNS.

The calculated band gap of pristine BNNS was 5.01 eV, consistent with previous reports [163]. Additionally, the HOMO-LUMO energy gap was found to be 5.87 eV, indicating a significant barrier to electron transfer and reflecting the inherently low conductivity of the material. Upon functionalization with PPPh, both the band gap and the energy gap significantly decreased to 2.84 eV and 2.86 eV, respectively, closely aligning with previously reported values [140]. This represents a 51% and 43% reduction in the energy and band gaps, respectively, suggesting a notable shift in the conduction and valence bands, which enhances electron mobility. The reduction in the HOMO-LUMO gap further indicates improved electron transfer and increased reactivity. Consequently, the effects of various electron-withdrawing groups (EWGs) and electron-donating groups (EDGs) on the band gap and energy gap of PPPh-BNNS were investigated, as shown in **Figure 3.3**.

Functionalization with electron-donating groups (EDGs) such as hydroxyl, amino, and methoxy groups showed minimal effects on the band gap. However, methyl group functionalization led to an increase in the band gap, likely due to steric hindrance, which distorts the polymer chain, alters conjugation planarity, and reduces conjugation. The methyl group's electron-donating nature increases the energy of the highest occupied molecular orbital (HOMO) and decreases the energy of the lowest unoccupied molecular orbital (LUMO), thereby widening the band gap. Additionally, methyl groups may interact with the π -orbitals of the polymer, further altering the electronic structure and contributing to this increase. A similar trend was observed for the energy gap.

In contrast, functionalization with EWGs such as carboxyl, cyano, and nitro groups led to a decrease in both the band gap and energy gap, with the nitro group exhibiting the lowest values at 2.09 eV and 2.11 eV, respectively. This corresponds to a decrease of 57% and 50% (carboxyl), 55% and 47% (cyano), and 63% and 58% (nitro) in energy and band gap, respectively. Halogen groups (fluoro, chloro, and bromo) showed negligible changes in these parameters. The carboxyl group facilitates intramolecular charge transfer and stabilizes the system through π - π interactions with neighboring polymer chains, leading to a reduced band gap. The cyano group induces polarization effects, increasing electron density on the polymer backbone and enhancing charge transport, which narrows the band gap. The nitro group, however, has a more pronounced impact. Its resonance interactions with the polymer's π -system delocalize electrons, extending conjugation and decreasing the band gap. Additionally, the nitro group's electron-withdrawing nature induces a partial positive charge on the benzene ring, forming a quinoid structure. This structure enhances conjugation along the backbone, facilitates intramolecular charge transfer, and further reduces the band gap [165].

These findings highlight the significant impact of the functional groups, particularly the nitro group, on the electronic as well as structural properties of PPPh-BNNS complexes. Based on these observations, adsorption studies were conducted on nitro-functionalized PPPh-BNNS complexes with various metals and ions, as illustrated in **Figure 3.4**.

Meanwhile, global reactivity descriptors, including chemical potential (μ), electronegativity (χ), hardness (η), softness (S), and electrophilicity (ω), were utilized to evaluate the impact of functionalization on BNNS, as presented in **Figure 3.5**. The chemical reactivity parameters were estimated using Parr and Pearson theories [166].

Chemical potential (μ) represents the tendency of electrons to escape from a system. Chemical hardness (η) quantifies a system's resistance to changes in charge density distribution and correlates strongly with its reactivity and stability [167]. According to the hard/soft acid/base (HSAB) theory, molecules with higher hardness values exhibit reduced reactivity, as they are less likely to donate electrons during interactions. In contrast, species with lower hardness values facilitate more efficient electron transfer. The electrophilicity index (ω), introduced by Parr et al. [166], is derived from chemical potential and hardness. This index measures the energy reduction associated with optimal electron transfer between donor and acceptor species, providing insights into the reactivity and stability of the system. These descriptors collectively offer a comprehensive understanding of the chemical behavior of functionalized BNNS.

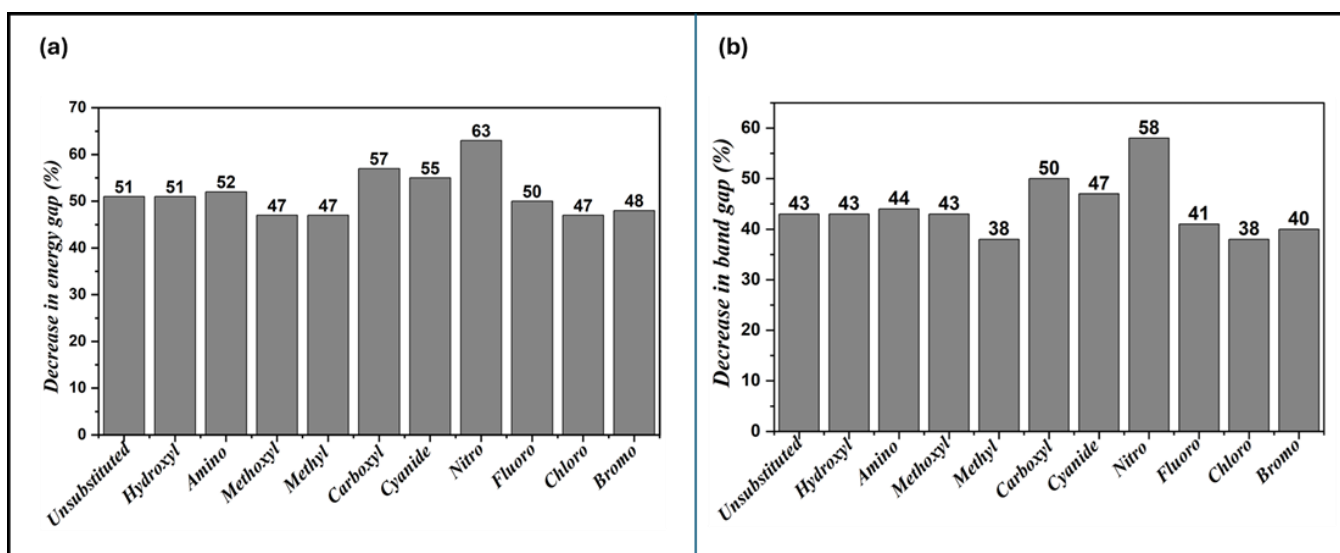


Figure 3.3 Calculated percentage decrease in (a) energy gap and (b) band gap of PPPh-BNNS, and various electron-withdrawing and electron-donating groups functionalized on PPPh-BNNS complexes.

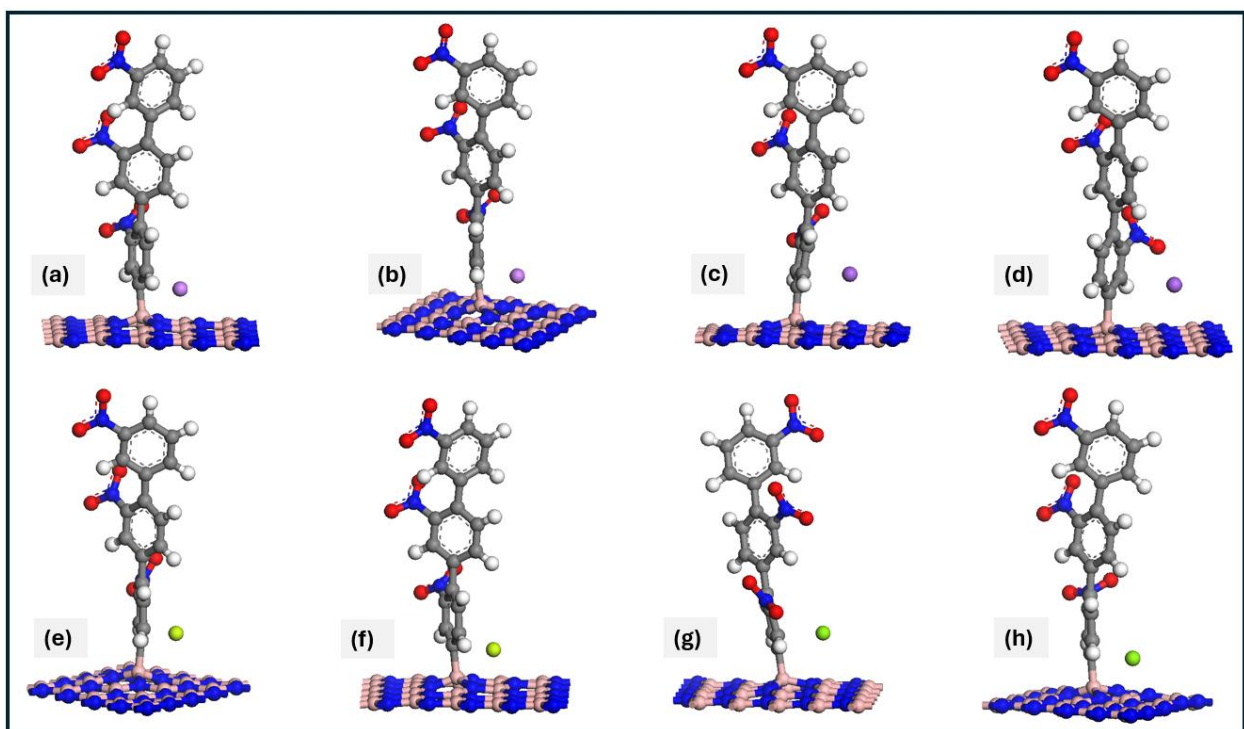


Figure 3.4 Optimized adsorption structures of various metals/ions on the promising nitro- group functionalized PPPh-BNNS complex namely (a) Li@PPPh-BNNS, (b) Li⁺@PPPh-BNNS, (c) Na@PPPh-BNNS, (d) Na⁺@PPPh-BNNS, (e) Be@PPPh-BNNS, (f) Be²⁺@PPPh-BNNS, (g) Mg@PPPh-BNNS, (h) Mg²⁺@PPPh-BNNS complexes.

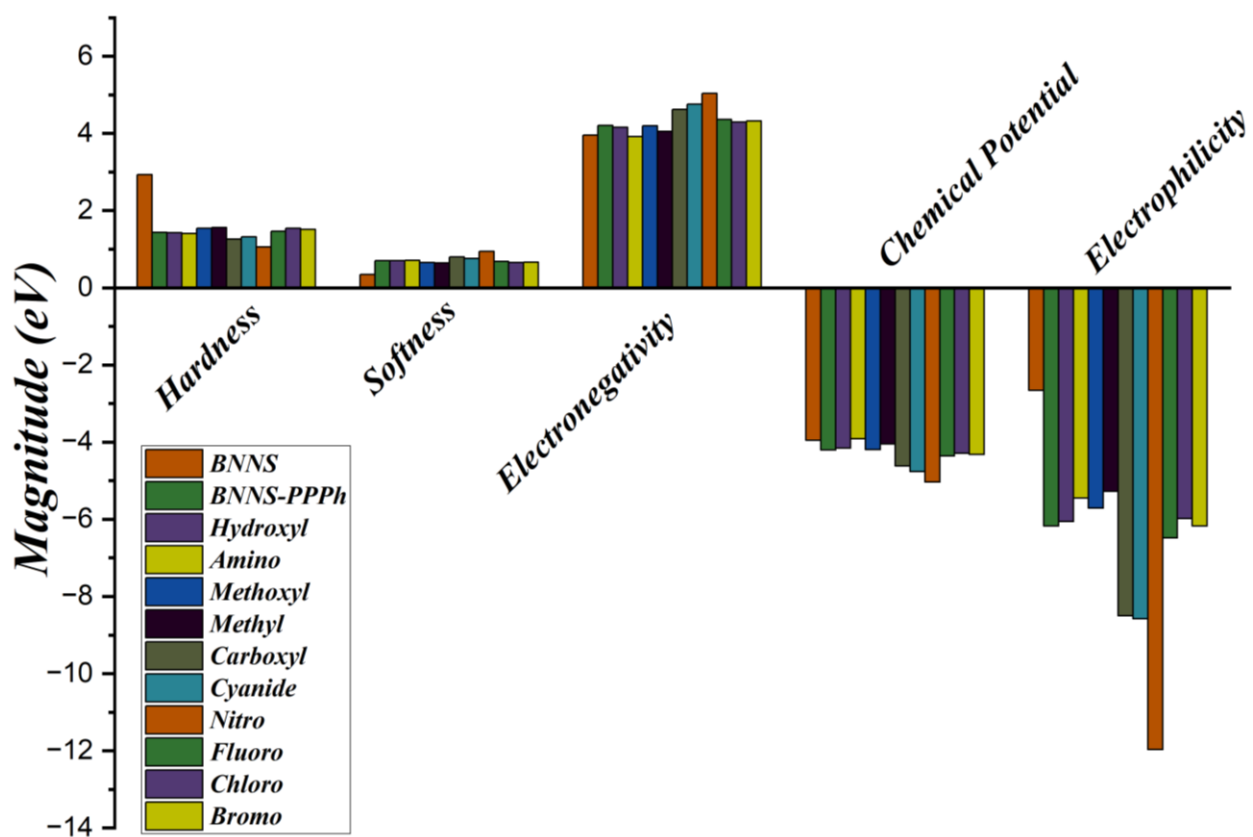


Figure 3.5 Comparison of the global reactivity descriptors of BNNS, PPPh-BNNS and EWG, and EDG functionalized PPPh-BNNS.

3.3.3 Adsorption of Li/Li⁺, Na/Na⁺, Be/Be²⁺ and Mg/Mg²⁺ on BNNS and PPPh-BNNS

The impact of various metals/ions on the electronic structure and properties of bare BNNS was previously discussed. Here, we summarize the nature of adsorption, focusing on the metal/ion-boron and metal/ion-nitrogen bond distances for different M/Mⁿ⁺ species on pristine BNNS and the nitro-group functionalized PPPh-BNNS. As shown in **Figure 3.6** and **Table 1**, species such as Li⁺@BNNS, Na⁺@BNNS, Be²⁺@BNNS, and Mg²⁺@BNNS exhibit shorter bond distances compared to their neutral metal counterparts. This can be attributed to the electrostatic attraction and smaller ionic radii of these cations, which allow for stronger coordination.

Upon functionalization with nitro-PPPh, these bond distances decreased further in most cases, though the overall trend remained consistent. This indicates that metal-ion complexes form shorter M-B or M-N bond distances compared to their neutral atomic counterparts, as detailed in **Table 1**. The reduction in bond distances upon nitro-PPPh functionalization could be attributed to the electron-withdrawing nature of nitro groups, which increases the positive charge on the carbon atoms of PPPh. This effect enhances π - π interactions and orbital overlap with BN, resulting in stronger electrostatic interactions between the metal cations and the functionalized BNNS. These interactions likely contribute to the enhanced stability of the system.

Additionally, the ΔE_{cell} and cell voltages generated by the adsorption of M/Mⁿ⁺ on BNNS and nitro-PPPh-BNNS are shown in **Figures 3.7 and 3.8** respectively. Adsorption energies, a critical factor in designing metal-ion batteries, were also analyzed. High adsorption energy values are associated with greater material stability during the electrochemical process [168]. Positive adsorption energy values indicate endothermic

formation with lower stability, whereas negative values denote exothermic formation and higher stability.

Our results align well with these findings. While positive adsorption energies were observed for M/M^{n+} on pristine BNNS, functionalization with nitro-PPPh led to negative adsorption energy values. This suggests that nitro-PPPh functionalization enhances metal/ion mobility and system stability. To further explore the impact of adsorption on the electronic structure, the total density of states (TDOS) and band structures for BNNS and nitro-PPPh-BNNS are presented in **Figure 3.9**.

Furthermore, the diffusion behavior of various metal ions across the sheet was estimated. The plot of mean square deviation versus the time steps showing the diffusion patterns across the PPPh-sheet is illustrated in **Figure 3.10**. The metal ions exhibited different diffusion behaviors. For instance, Na^+ prefers to diffuse on a linear pathway and has the highest diffusion coefficient value of $1.0 \text{ cm}^2/\text{s}$, indicating the easier movement of sodium ions over other ions across the complexes. The higher diffusion coefficient of sodium ions can be attributed to the relative larger ionic radius and lower charge density, resulting in weaker interactions with the functionalized 2D boron nitride nanosheet. The diffusion coefficient values of Li^+ , Be^{2+} and Mg^{2+} was calculated to be 0.10, 0.25 and $0.14 \text{ cm}^2/\text{s}$, respectively. Furthermore, these ions shows non-linearity in their diffusion patterns. The observed non-linear diffusion patterns of Li, Be, and Mg ions are likely due to their stronger electrostatic interactions and specific binding sites with the functionalized nanosheet, whereas sodium ions exhibit linear diffusion due to their relatively weaker interactions.

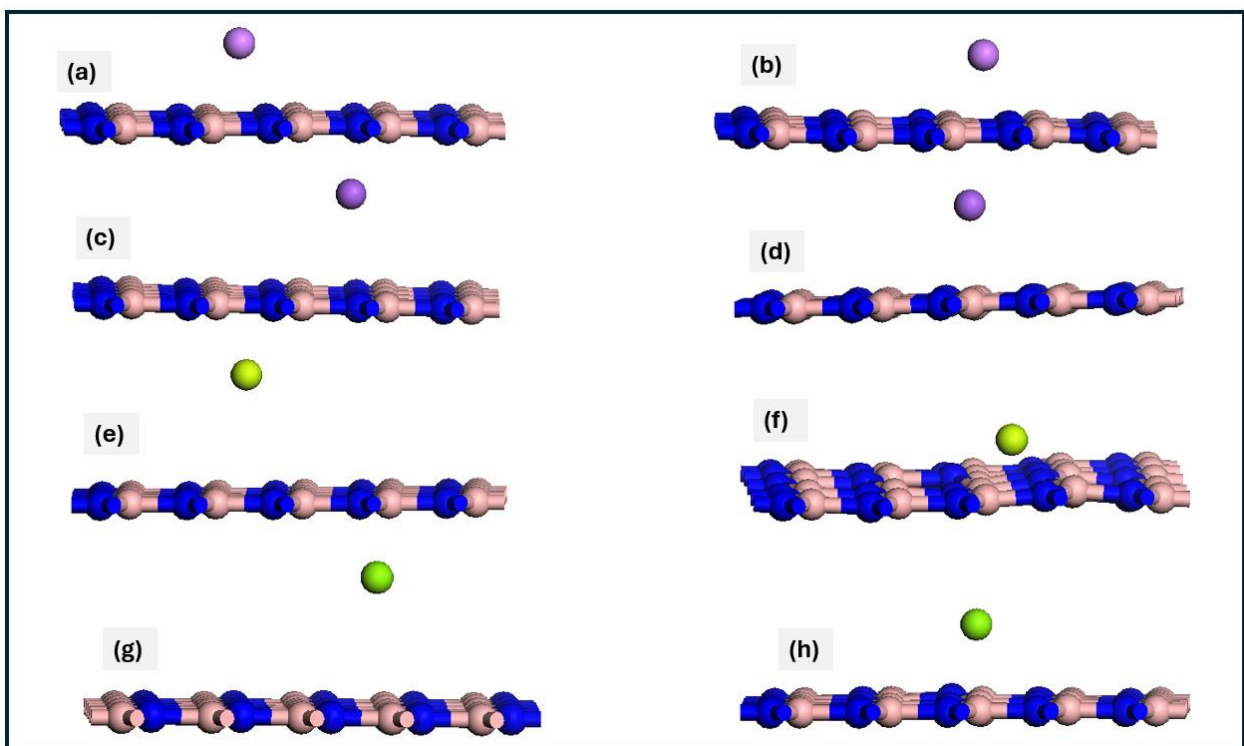


Figure 3.6 Cross-sectional view of Optimized structures of (a) Li@BNNS, (b) Li⁺@BNNS, (c) Na@BNNS, (d) Na⁺@BNNS, (e) Be@BNNS, (f) Be²⁺@BNNS, (g) Mg@BNNS, (h)Mg²⁺@BNNS

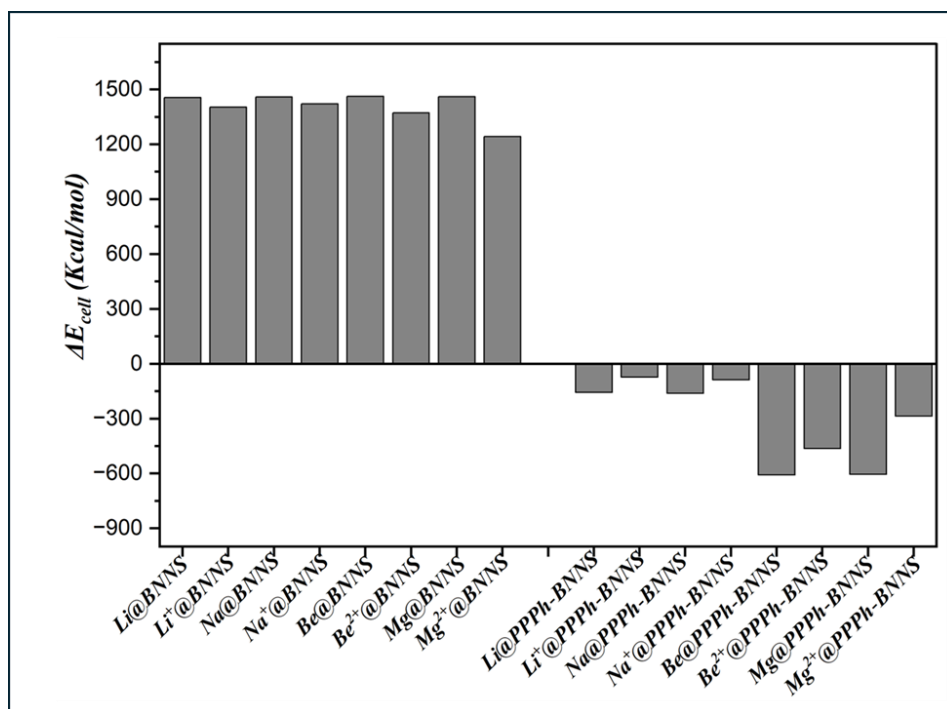


Figure 3.7 Depicts the calculated cell energies (ΔE_{cell}) of M/Mn+@BNNS and M/Mn+@PPPh-BNNS.

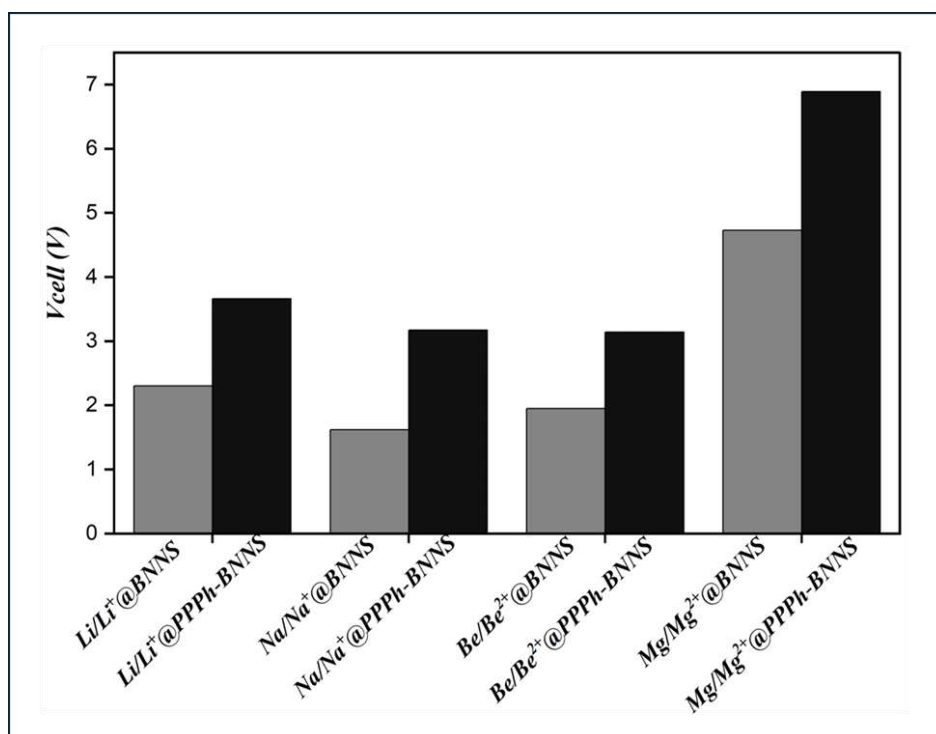


Figure 3.8 The calculated cell energies (ΔE_{cell}) of M/Mn+@BNNS and M/Mn+@PPPh-BNNS.

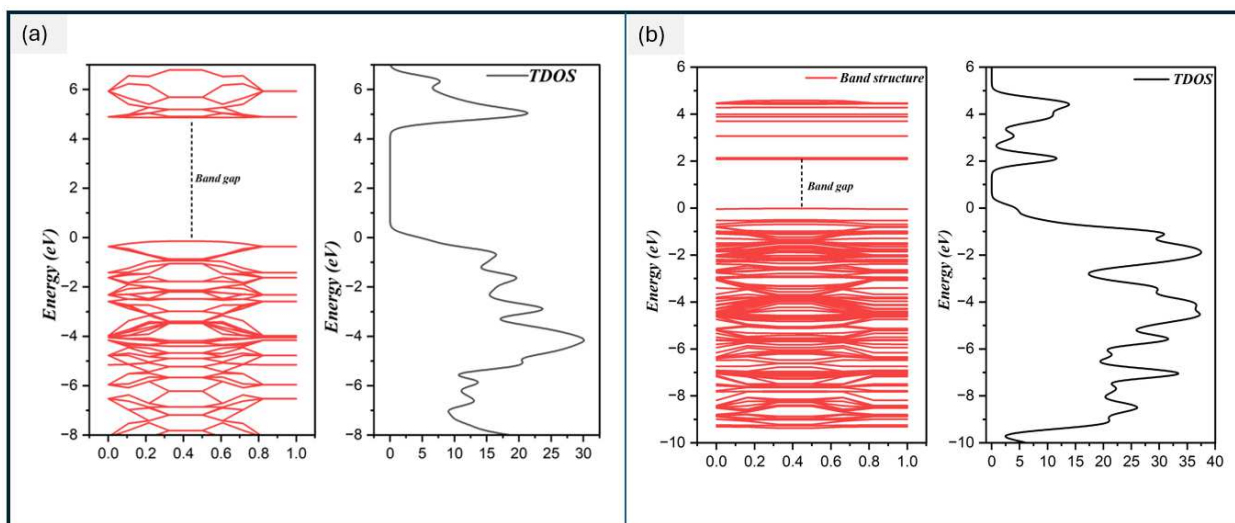


Figure 3.9 The band structure and total density of state of (a) bare BNNS and (b) nitro-group functionalized PPPh-BNNS showcasing the gap between the conduction and valence band before and after functionalization.

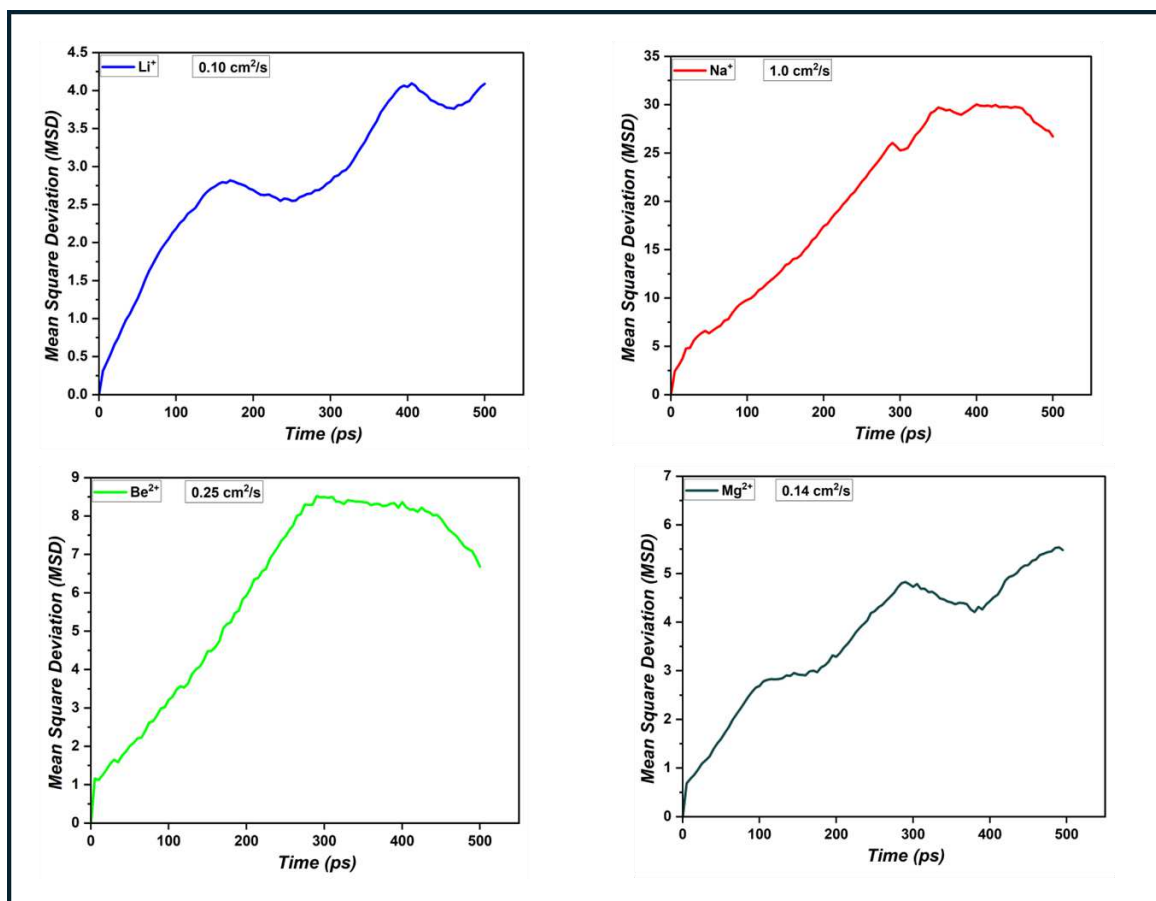
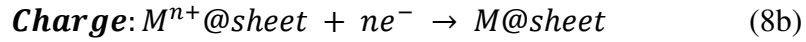
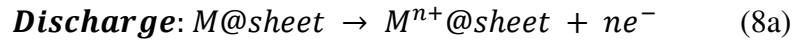
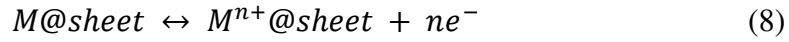


Figure 3.10 Diffusion pattern of various metal ions across the nanosheet

3.3.4 Ion battery Application of BNNS and nitro-PPPh-BNNS

The BNNS and nitro-PPPh-BNNS act as anodes for ion batteries. Generally, electrochemical reactions occurring at the anodic and cathodic half cells are detailed in Equations 5 and 6, consistent with literature reports [140,169,175]. The overall cell reaction is presented as follows.

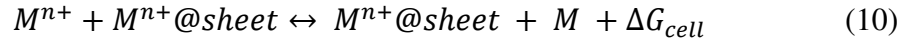
At anode:



At cathode:



Overall cell reaction:



Where M, M^{n+} , and sheet denote the metal atoms, the metal ions, and the BNNS and/or nitro-PPPh-BNNS, respectively

Table 2. presents the HOMO, LUMO, and adsorption energy values of pristine BNNS and functionalized BNNS. The positive adsorption energy of M/ M^{n+} @BNNS indicates weaker interactions between the metal/metal ions and the BNNS electrode system. Conversely, the negative change in internal energy observed with nitro-PPPh functionalization signifies stronger interactions, enhanced electron diffusion, and extended cycle life [168]. This

underscores the critical role of the nitro-PPPh functionalized substrate in improving metal/ion interactions and increasing cell voltages.

Figure 3.8 illustrates the predicted cell voltage (V_{cell}) values for $M/M^{n+}@BNNS$ and $M/M^{n+}@nitro-PPPh-BNNS$ systems. The results show that cell voltage is influenced by the charge density and size of the adsorbed metal atoms or ions. For alkali metals/ions, a decreasing trend in cell voltage is observed moving down the group, with $Li@BNNS$ and $Na@BNNS$ yielding cell voltages of 2.30 V and 1.62 V, respectively. The optimal computed cell voltages for lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs) are 3.66 V and 3.18 V, respectively, aligning well with previously reported values [140,170]. In contrast, for alkaline earth metals/ions, the cell voltage increases down the group. This trend is attributed to the decreasing ionic radius, which strengthens electrostatic attractions within the electrode system. For instance, the cell voltages for $Be^{2+}@BNNS$ and $Mg^{2+}@BNNS$ were calculated as 1.95 V and 4.73 V, respectively. After functionalization with nitro-PPPh, these values increased to 3.14 V and 6.89 V, respectively.

Overall, functionalizing BNNS with conducting polymers such as nitro-PPPh significantly improves the material's electrochemical performance. This modification reduces the gap between conduction and valence bands, enhances conductivity, increases the electroactive surface area, and lowers interfacial resistance. These improvements lead to enhanced electrochemical reversibility of metal ions at the electrodes, resulting in better battery performance, faster charge/discharge rates, and an extended life cycle [140].

Table 3.2 Calculated HOMO, LUMO, energy gap, % change in energy gap, and adsorption energies of metals and metal ions on BNNS and PPPh-BNNS complexes compared to the bare BNNS and functionalized BNNS structures.

Complex	E _{HOMO} (eV)	E _{LUMO} (eV)	Energy gap (E _g) (eV)	%ΔE _g (eV)	E _{ad} (Kcal/mol)
BNNS	-6.89	-1.01	5.87	-	-
Li@BNNS	-6.64	-1.95	4.68	-20.22	1456.46
Li ⁺ @BNNS	-7.54	-2.91	4.62	-21.19	1403.33
Na@BNNS	-6.64	-2.30	4.34	-26.03	1458.82
Na ⁺ @BNNS	-7.27	-3.41	3.86	-34.14	1421.38
Be@BNNS	-5.43	-1.82	3.61	-38.39	1463.12
Be ²⁺ @BNNS	-9.04	-6.79	2.25	-61.63	1373.00
Mg@BNNS	-4.57	-1.42	3.15	-46.26	1461.29
Mg ²⁺ @BNNS	-8.62	-7.84	0.78	-86.63	1242.94
BNNS-PPPh	-6.09	-3.97	2.11	-63.94	-
Li@BNNS-PPPh	-5.97	-4.19	1.78	-69.64	-156.75
Li ⁺ @BNNS-PPPh	-6.74	-4.42	2.32	-60.47	-72.34
Na@BNNS-PPPh	-6.49	-4.36	2.12	-63.78	-161.14
Na ⁺ @BNNS-PPPh	-6.56	-4.90	1.66	-71.70	-87.87
Be@BNNS-PPPh	-6.52	-4.61	1.91	-67.34	-607.81
Be ²⁺ @BNNS-PPPh	-7.10	-4.46	2.63	-55.09	-462.86
Mg@BNNS-PPPh	-4.78	-4.37	0.40	-93.10	-603.58
Mg ²⁺ @BNNS-PPPh	-7.08	-5.20	1.88	-67.83	-285.61

3.3.5 Work function

The work function (Φ) represents the minimum energy required to remove a single electron from the Fermi level [158], serving as a critical parameter for estimating the potential barrier of electron emission from solids or molecules. This property significantly influences charge transfer kinetics [172]. In materials such as BNNS, Φ plays a pivotal role, highlighting the potential of these materials as electrodes in electronic devices, including organic light-emitting diodes (OLEDs), touch screens, and solar cells [173]. Accordingly, we compare the estimated Φ of various metals on the promising nitro-PPPh functionalized BNNS with the carboxy-PPPh and cyano-PPPh functionalized BNNS which are denoted as BNNS-PPPh-NT, BNNS-PPPh-CB and BNNS-CY respectively as illustrated in **Figure 3.11**.

The calculated Φ values for M@BNNS-PPPh-nitro range from 2.09 to 2.30 eV which is of lower values than the M@BNNS-PPPh-cyano and M@BNNS-PPPh-carboxy. The notably low value of Φ suggest decrease energy barrier for ion intercalation and deintercalation, facilitating easier ion movement between the electrode [174]. Furthermore, a lower Φ reduces electrochemical polarization which is the difference between electrode potential and equilibrium potential, thus improving life cycle by reducing the mechanical stress which enhance electrochemical stability and high-rate performance. On contrary, high values of Φ hinders electron transfer which results in reduced battery efficiency, increases internal resistance and decrease overall battery performance [176]. Generally, the study shows the functionalization of BNNS with nitro-PPPh enhances charge transfer kinetics, electrochemical stability, and the voltage window, while promoting optimal cycle life and material stability.

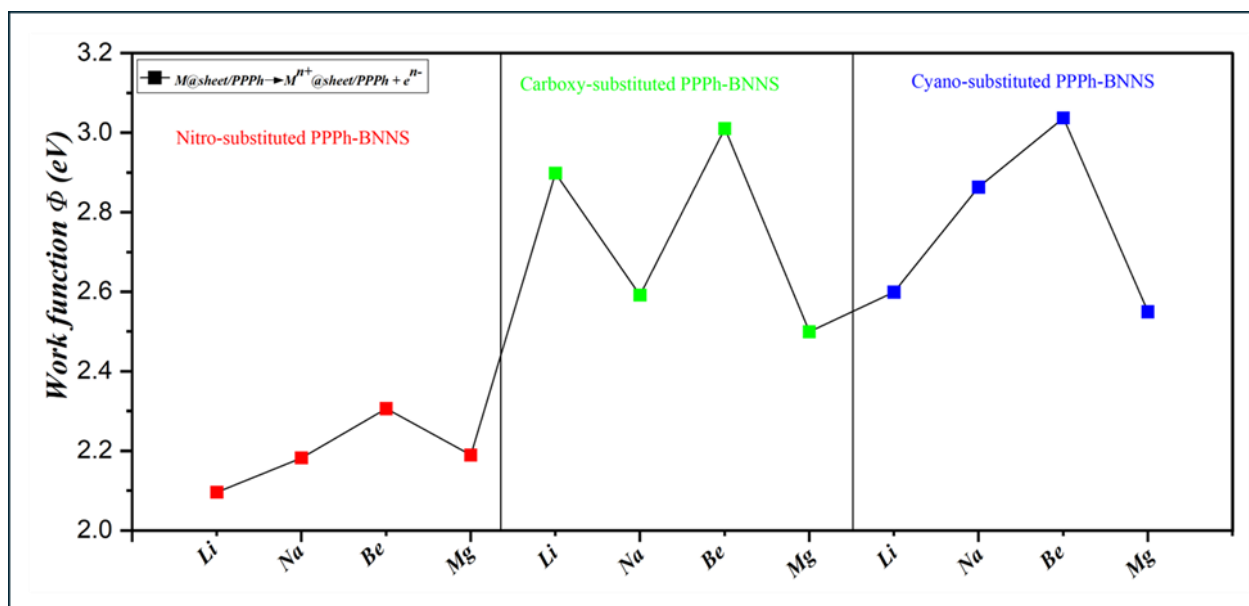


Figure 3.11 Calculated work function (Φ) of various M@BNNS-PPPh-nitro, M@BNNS-PPPh-carboxy, and M@BNNS-PPPh-cyano complexes.

3.3.6 Thermal stability.

A critical property influencing the suitability of materials for high-temperature applications is their ability to maintain structural integrity within specific temperature ranges. Elevated temperatures, often caused by various reactions within batteries, can induce distortions in electrode materials, thereby reducing the overall lifespan of the battery. Therefore, assessing the thermal stability of electrode materials is essential. In this study, dynamic simulations were conducted to evaluate the thermal stability of BNNS and nitro-PPPh-BNNS, as presented in **Figure 3.11**.

The simulations utilized a $5 \times 5 \times 1$ supercell with a time step of 0.5 fs for 2000 total steps, corresponding to a simulation duration of 1 ps at 300 K and 500 K. For pristine BNNS, slight fluctuations in potential energy were observed at 300 K, with the structure maintaining its configuration. At 500 K, fluctuations persisted with a noticeable drift in potential energy, though the structural integrity remained intact. Following functionalization with nitro-PPPh, a significant reduction in fluctuations and stable potential energy was observed at both 300 K and 500 K.

This enhanced stability can be attributed to the interaction between the aromatic ring system of PPPh and the hexagonal lattice of BNNS, which mitigates thermal expansion. Additionally, defect passivation by the nitro group in PPPh likely minimizes thermal energy transfer. These findings indicate that functionalized BNNS exhibits improved thermal stability, making it a promising anodic material for high-temperature applications.

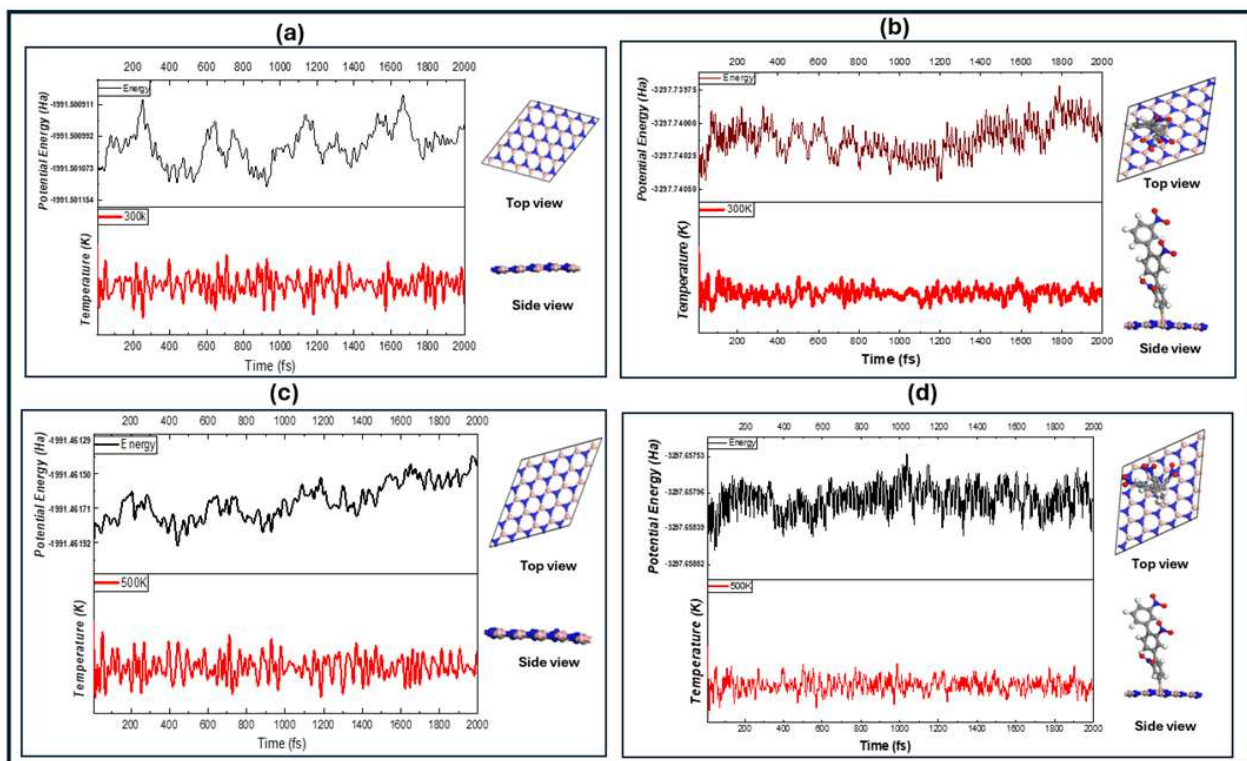


Figure 3.12 The simulated dynamics temperature and potential energy fluctuations with the corresponding final geometrical structures of (a) bare BNNS @300k, (b) PPPh-BNNS @300K, (c) bare BNNS @500k and (d) PPPh-BNNS @500k

3.3.7 Open circuit voltage and theoretical specific capacity

Open circuit voltage (OCV) is a pivotal metric in evaluating the performance of metal ion batteries. It provides insight into the thermodynamics and electrochemical behavior of battery materials. Herein, we extend our study in estimating the theoretical capacity and average open circuit of LIB and NIB which are the most established metal ion batteries. OCV is often calculated from the Nernst equation ($\frac{-\Delta G}{zF}$). However, since the entropy, and volume effect are considered negligible at room temperature [177], the OCV can be estimated from the differences in adsorption energies of the metals using the equation below [178]:

$$\text{OCV} = \frac{-[E_{M_x\text{PPPh}/\text{BNNS}} - (x - x_0)E_M - E_{\text{Li}_{x_0}\text{PPPh}/\text{BNNS}}]}{(x - x_0)} \quad (11)$$

Where $\text{PPPh}/\text{BNNS}, E_M$ is and $(x - x_0)$ represent the nitro-PPPh functionalized BNNS, the energy of an isolated metal atom, and the number of metal atoms taking part in the reaction per unit formula respectively. Similarly, to establish the OCV profile, the formation energies were used to investigate the stabilities of the intermediate structures through the injection of 1 to 10 metal atoms **Fig. 3.13 and 3.14**. Thus, the formation energies of the intermediate structures were estimated using the equation below:

$$E_{if} = E_{M_x\text{sheet}/\text{poly}} - \frac{(xE_{M_{10}\text{PPPh}/\text{BNNS}} + (10-x)E_{\text{PPPh}/\text{BNNS}})}{10} \quad (12)$$

Where E_{if} and x are the intermediate formation energy and the number of substituted metal atoms respectively.

The convex hull plot for the intermediate phase formation is illustrated in **Figure 3.15a&b**.

For the $\text{Li}_x\text{BNNS-PPPh}$ system, four intermediate phases ($x = 3, 4, 5$, and 7) were identified

as thermodynamically unstable. In contrast, the Na_xBNNS-PPPh counterpart exhibited three unstable intermediate phases at $x = 3$, 4, and 9. Since metal interaction calculations are based solely on phases lying on the convex hull, these unstable intermediate structures were excluded from further analysis [177]. The open-circuit voltage (OCV) profile is depicted in **Figure 3.15c-d**. During the lithiation process, a significant voltage drop was observed, decreasing from 4.6 V at $x = 1$ to 3.3 V at $x = 2$, followed by a further decline to 2.2 V at $x = 6$. Similarly, in the sodiation process, a sharp reduction in voltage was recorded, from 3.9 V at $x = 1$ to 2.9 V at $x = 2$. These pronounced voltage drops can be attributed to the strong electrostatic interactions between the metal ions and the BNNS framework. Overall, the OCV profile exhibits a decreasing trend as the number of intercalated metal atoms increases. At a specific metal-ion concentration, the discharge voltage stabilizes, indicating the system's maximum energy storage capacity. The calculated average open-circuit voltages (OCVs) for the designed lithium-ion battery (LIB) and sodium-ion battery (SIB) systems are 2.73 V and 2.28 V, respectively, surpassing the values reported for previously studied materials (**Table 3.3**).

The theoretical specific capacity is a key parameter for assessing the electrochemical performance of electrode materials, as it quantifies the energy storage capacity per unit mass. It is typically calculated using the following equation [178]:

$$C_m = \frac{xF}{M}$$

Where C_m is the specific capacity, x is the number of electrons involved in the electrochemical process, F is the Faraday constant and M is the molar mass of nitro-PPPh-BNNS.

The calculated maximum specific capacities for the proposed LIBs and SIBs are 244 mAh/g and 217 mAh/g, respectively. While these values are lower than those of commercial graphene [179], they exceed the specific capacities reported for MoS₂ [180] and MoC₂ [181]. This indicates that BNNS-functionalized PPPh-based electrodes exhibit promising electrochemical characteristics, particularly for high-voltage applications requiring stable and efficient charge storage.

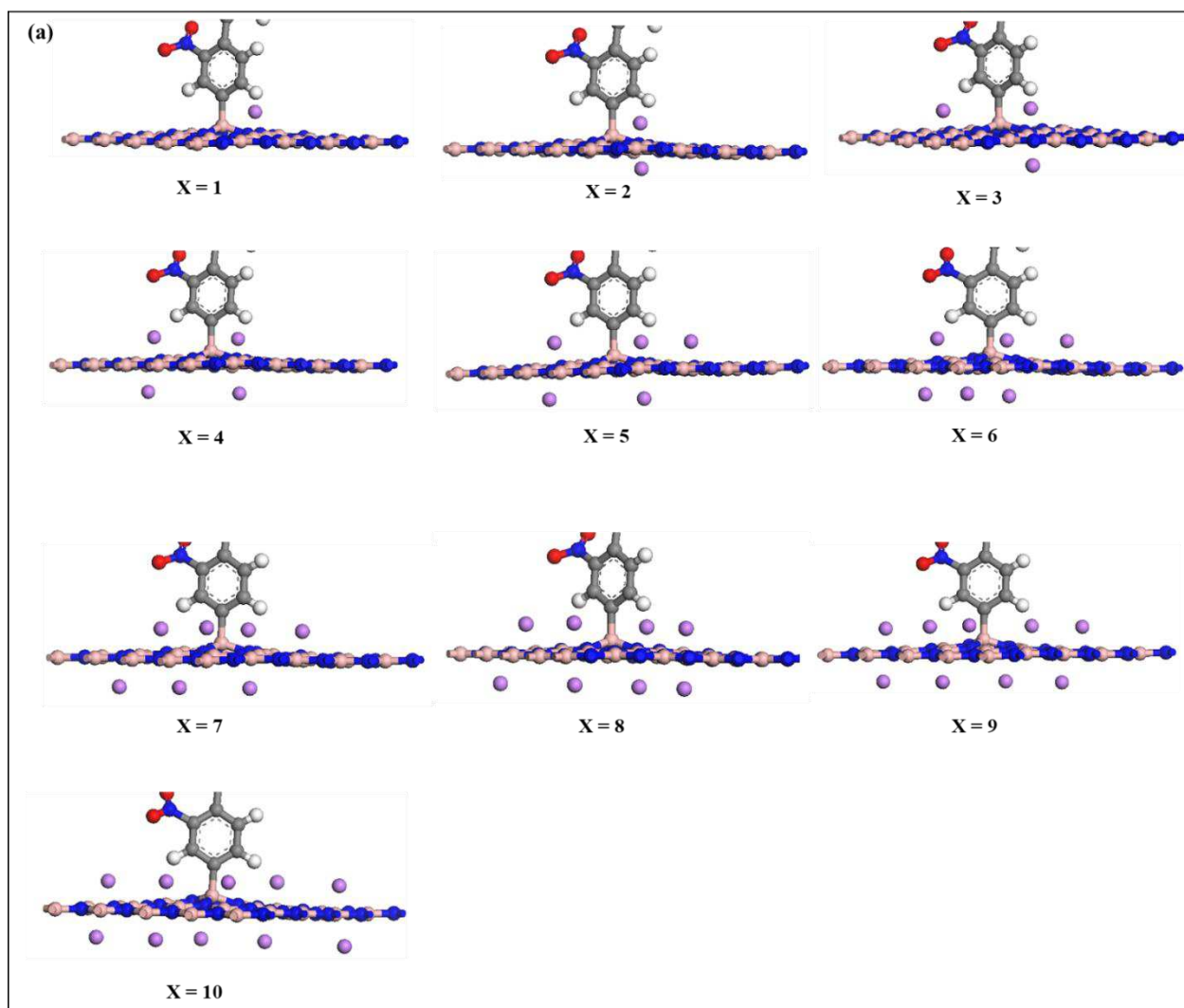


Figure 3.13 Configurations of $\text{Li}_x\text{BNNS-PPPh}$ with Li binded on both side of the boron nitride nanosheet.

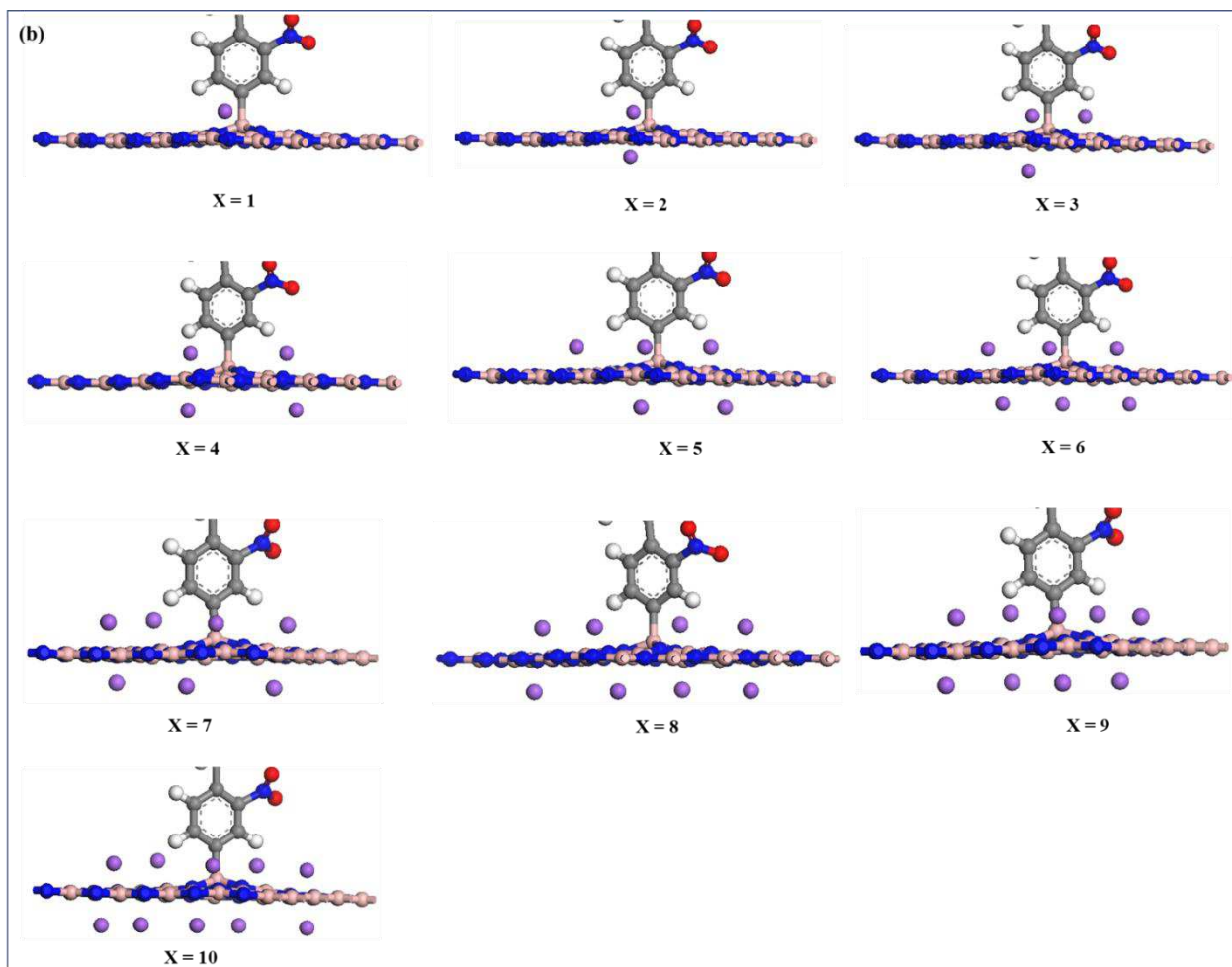


Figure 3.14 Configurations of $N_xB_{10}N_{10}S$ -PPPh with Li bonded on both sides of the boron nitride nanosheet.

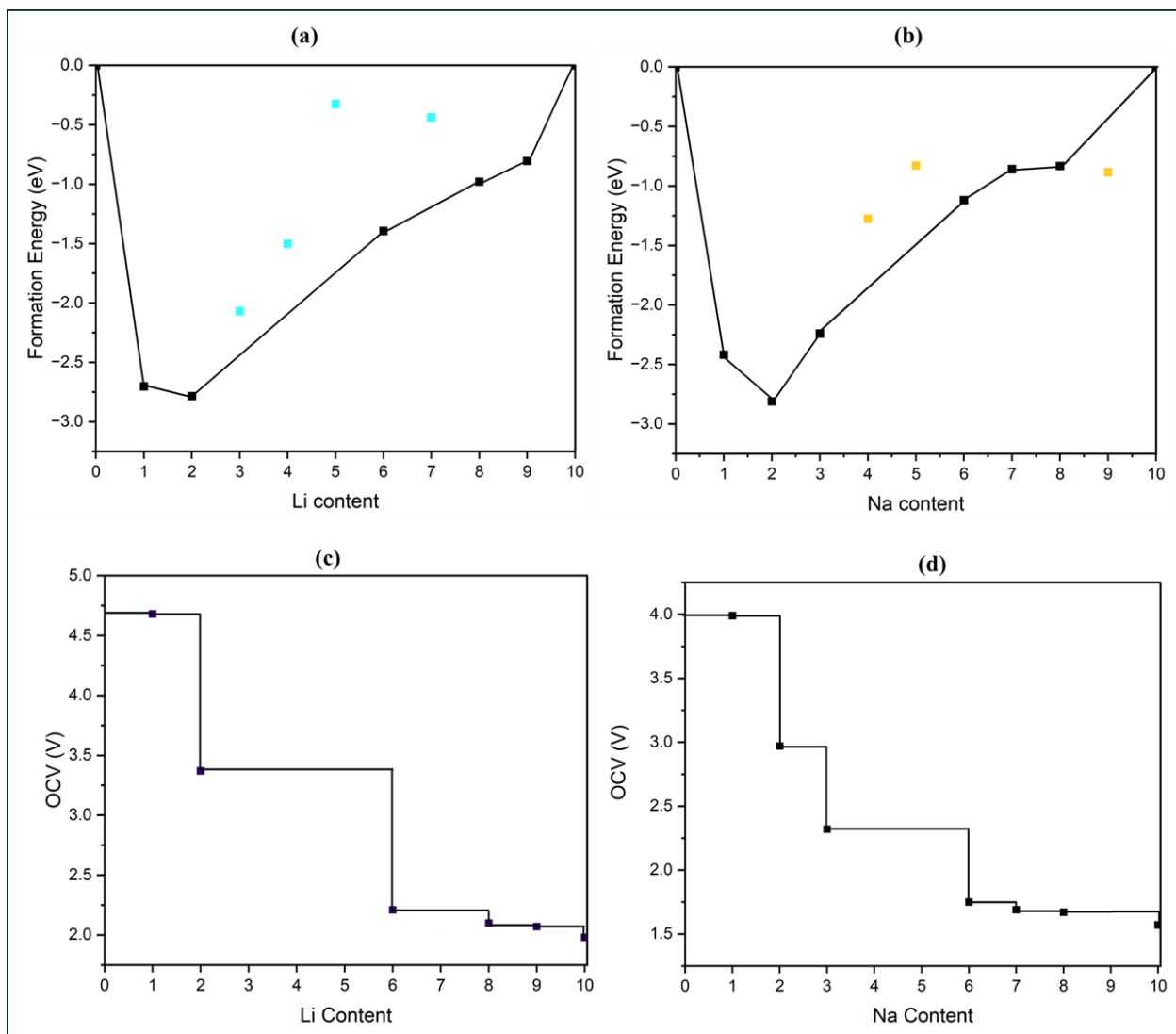


Figure 3.15 The intermediate formation energies of (a) $\text{Li}_x\text{BNNS-PPPh}$ (b) $\text{Na}_x\text{BNNS-PPPh}$, and the corresponding voltage profile of (c) $\text{Li}_x\text{BNNS-PPPh}$ and (d) $\text{Na}_x\text{BNNS-PPPh}$, with respect to Li and Na content from 0 to 10.

Table 3.3 . Comparison of open-circuit voltage (OCV), and theoretical specific capacity (C_m) of some anode materials in lithium and sodium battery applications.

Anode material	OCV	C _m	Ion battery	Ref.
PPPh-BNNS	2.73	244	LIB	This work
PPPh-BNNS	2.28	217	SIB	
Mxene (Ti ₃ N ₂)	0.58	312	LIB	[182]
MoS ₂	1.25	146	SIB	[180]
graphene	-	~372	LIB	[179]
GeS nanosheet	0.20	256	LIB	[183]
MoC ₂	0.166	132	SIB	[181]
Nb ₂ C	0.27	271	SIB	[184]
VS ₂	0.93	466	LIB	[185]

CHAPTER 4

FUNCTIONALIZATION OF BORON CARBON NITRIDE NANOSHEETS WITH CONDUCTING POLYMERS: A STRATEGY TO BALANCE CONDUCTIVITY AND ELECTROCHEMICAL PERFORMANCE IN METAL ION BATTERIES

4.1 Introduction

The escalating global demand for renewable energy storage systems, driven by the rapid growth of portable electronics, electric vehicles, and grid-scale energy storage, has intensified research into advanced rechargeable battery technologies. Lithium-ion batteries (LIBs) have dominated the market due to their high energy density and long cycle life [186]. However, the finite nature and geographic mismatch of lithium resources, coupled with growing interest in post-lithium systems such as sodium- (SIBs), beryllium- (BIBs), and magnesium-ion batteries (MIBs), have necessitated the search for high-performance anode materials adaptable to different alkali and alkaline earth metal ions [187-188]. While highly successful for LIBs, traditional graphite anodes are beset by poor kinetics and a dearth of interlayer spacing for larger ions (e.g., Na^+ , Mg^{2+}) [189], which has driven the search for new materials with enhanced ion adsorption, conductivity, and structural integrity.

Two-dimensional (2D) materials, such as graphene, transition metal dichalcogenides (TMDs), and hexagonal boron nitride (h-BN), have emerged as promising candidates due to their high surface area, tunable electronic properties, and mechanical robustness [190]. Boron carbon nitride (BCN) nanosheets, a ternary hybrid of graphene and h-BN, combine the advantages of both materials, offering a unique electronic structure, chemical stability, and rich surface chemistry [191]. Recent studies by Kaur et al. [192] demonstrated that

BCN nanosheets exhibit exceptional thermal stability and ion adsorption capabilities, while Cheng et al. [193] highlighted their potential as LIB anodes with a capacity of 800 mAh/g. However, the intrinsically small bandgap ($\sim 0 - 2$ eV) of BCN nanosheets poses a critical challenge: near-metallic conductivity may lead to undesirable electron leakage during charge/discharge cycles, reducing Coulombic efficiency and cycling stability [194-195]. This challenge is similar to what has been observed in graphene-based anodes, where metallic properties often lead to dendrite formation and gradual capacity loss [196]. To overcome these limitations, further research is needed to optimize BCN nanosheets for energy storage applications and address these performance issues. One promising approach involves functionalization strategies that fine-tune electronic properties while maintaining ion-accessible surfaces. Conducting polymers, such as poly(para-phenylene) (PPP), have gained attention for their adjustable conductivity, mechanical flexibility, and ability to work synergistically with inorganic nanomaterials [197]. For instance, Natthakan et al. [198] reported that polypyrrole-coated graphene composites showed improved Li^+ adsorption due to enhanced interfacial charge transfer. Similarly, Chidera et al. [199] demonstrated that polythiophene- and polypyrrole-functionalized h-BN provided stable metal ion storage through π - π interactions between the polymer and the 2D substrate. Building on these advancements, functionalizing BCN nanosheets with poly-p-phenylene (PPPh) presents a dual benefit. The polymer's conjugated π -system can stabilize the electronic structure of BCN, reducing its metallic behavior, while the hybrid architecture enhances ion adsorption through tailored interfacial interactions. This combination could pave the way for more efficient and stable energy storage solutions.

Incorporating electron-withdrawing groups (EWGs), such as $-\text{NO}_2$ and $-\text{CN}$, or electron-donating groups (EDGs), like $-\text{NH}_2$ and $-\text{OCH}_3$, at the meta-position of PPPh can provide precise control over the electronic environment. This, in turn, optimizes charge transfer kinetics and ion binding energetics. Such modifications are especially crucial for multivalent ions like Be^{2+} and Mg^{2+} , where strong Coulombic interactions can cause slow diffusion and structural degradation [200].

Recent studies have shown that EWG-functionalized polymers can enhance metal ion adsorption on 2D materials by polarizing surface charges, while EDGs can improve ion mobility in covalent organic frameworks [201-202]. However, there is still a lack of systematic research exploring how substituent chemistry, bandgap engineering, and multivalent ion storage interact in polymer-functionalized 2D hybrids. This gap presents a challenge in the rational design of anode material

In this study, we employ density functional theory (DFT) to systematically investigate the structural, electronic, and adsorption properties of BCN-PPPh hybrid systems as universal anode materials for Li^+ , Na^+ , Be^{2+} , and Mg^{2+} storage. By analyzing the role of EWGs and EDGs on the polymer backbone, we elucidate how substituent-induced charge redistribution modulates ion adsorption strength, diffusion barriers, and theoretical capacity. Our computational approach builds on recent DFT successes in predicting ion storage mechanisms in 2D materials [203-205] but extends these frameworks to ternary hybrids with polymer functionalization. The results reveal that functionalization not only rectifies the near-zero bandgap of pristine BCN but also creates ion-specific binding sites, enabling high-rate performance and stability across monovalent and multivalent systems. This work bridges the gap between material innovation and the evolving demands of next-

generation battery technologies, offering a foundational framework for designing polymer-functionalized 2D heterostructures as versatile anodes.

4.2 Computational methods.

All calculations were performed using the DMol3 module in Material Studio software [148]. The electron exchange-correlation energy was computed using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA), which is known for its accuracy in predicting electronic properties and adsorption energies [149-152]. To capture long-range van der Waals interactions, the Grimme dispersion correction (DFT-D3) was applied [153-155]. A smearing value of 0.005 Ha was used to determine orbital occupancy. The double numerical plus polarization (DNP) basis set was chosen to describe the valence electrons and accurately measure electrostatic interactions. Structural optimization was performed with parameters set for displacement, maximum force, and self-consistent field (SCF) at 0.002 Å, 0.001 Ha/Å, and 1.0×10^{-6} Ha, respectively, with a global orbital cutoff at 5.2 Å to ensure high accuracy and energy convergence. To avoid artificial interactions between neighboring layers due to periodic boundary conditions, a vacuum space of about 20 Å was introduced.

The adsorption energies of metal atoms/ions (M/Mⁿ⁺) on the bare BCNNS and poly-p-phenylene functionalized BCNNS (BCNNS-PPPh) were determined using the following equation:

$$E_{ad} = E_{complex} - [E_{sheet/PPPh-BCNNS} + E_{(M/M^{n+})}] \quad (1)$$

Here, E_{ad} , $E_{complex}$, $E_{sheet/PPPh-BCNNS}$, and $E_{(M/M^{n+})}$ denote the adsorption energy, the energy of the metal atoms/ions adsorbed on BCNNS or PPPh-BCNNS, the energy of the bare BCNNS or PPPh-BCNNS, and the energy of the isolated metal atoms/ions, respectively. Additionally, changes in the HOMO-LUMO energy gap (ΔE_g) resulting from the adsorption of various metal atoms/ions on the bare BCNNS and/or PPPh-BCNNS were calculated to evaluate the strength of interaction and adsorption sensitivity, as illustrated below:

$$\%E_g = \left[\frac{E_{g_{complex}} - E_{g_{sheet}}}{E_{g_{sheet}}} \right] \times 100\% \quad (2)$$

where E_g , $E_{g_{complex}}$ and $E_{g_{sheet}}$ represent the HOMO-LUMO energy gaps of the bare BCNNS or PPPh-BCNNS, the energy gap of the complex, and the energy gap of the bare sheet after the adsorption of metal atoms/ions ($E_{M/M^{n+}}$) respectively.

In addition, initial cell voltages (V_{cell}), was computed similarly to our previous work [140] using the Nernst equation below:

$$V_{cell} = \frac{-\Delta G_{cell}}{zF} \quad (3)$$

where V_{cell} , ΔG_{cell} , z , and F represents the initial cell voltage, Gibbs free energy, the charge on the metal ions (the electrolytic cations) and F is the Faraday's constant with the value of (96500 C/mol or 23.061 kcal/volt.mol). As depicted in Equation 4:

$$\Delta G_{cell} = \Delta E_{cell} + P\Delta V - T\Delta S \quad (4)$$

Since the contributions of entropy and volume effects are considered negligible ($<0.01V$) [29], the Gibbs free energy (ΔG_{cell}) which represents the energy of the overall cell reactions being studied, can be approximated as nearly equal to the change in internal energy [156].

Here, ΔE_{cell} refers to the change in adsorption energy of the bare BCNNS and/or PPPh-BCNNS under investigation.

The work function (Φ) is a crucial parameter that provides information about the minimum energy needed to remove an electron from the Fermi level [157-158]. For materials based on conductors and semiconductors, Φ can be used to assess their suitability as electrodes in electronic devices and solar cells [159-160]. Following the theoretical approach proposed by Wu et al. [159], the work function was calculated using the equation below.

$$\Phi = V_{el(+\infty)} - EF \quad (5)$$

$$EF = \left[\frac{E_{HOMO} - (E_{HOMO} - E_{LUMO})}{2} \right] \quad (6)$$

where E_{HOMO} , E_{LUMO} , EF , and $V_{el(+\infty)}$ denote the energies of the highest occupied molecular orbital, the energy of the lowest unoccupied molecular orbital, the energy of Fermi level, and the energy of the electron outside the surface of the metal/ion-BCNNS or PPPh-BCNNS systems. Since $V_{el(+\infty)} = 0$. Therefore, Φ was estimated as:

$$\Phi = -EF \quad (7)$$

Thermal stability refers to the temperature range within which a material remains intact without deformation, making it a crucial property for high-temperature applications. The thermal stability of the anodic material was evaluated using dynamics simulations at different temperatures on the DMol³ module.

4.3 Results and discussion

4.3.1 Structural optimization and electronic properties.

To explore the anodic performance of BCNNS and the effects of functionalization, hexagonal BCNNS, poly-p-phenylene (PPPh), and selected electron-donating (EDG) and electron-withdrawing groups (EWG) such as hydroxyl, amino, methyl, carboxyl, cyano, nitro, fluoro, chloro, and bromo were modeled and optimized (**Figure 1**). The BCNNS unit cell, consisting of boron, carbon, and nitrogen atoms, had a lattice parameter of $a=b=5.645$ Å, aligning with previous findings [206]. A (5×5) supercell, consisting of 50 atoms (17 boron, 17 carbon, and 16 nitrogen atoms), was utilized for structural analysis. The EWG and EDG groups were attached to the meta positions of three repeat units of PPPh (**Figure 4.1. d–m**), while the conductivity, charge carrier mobility, and anodic voltage of the functionalized BNNS system were evaluated.

The formation energies of BCNNS functionalized via PPPh attachment to boron, carbon, and nitrogen atoms were calculated. The average formation energies were -1.053, -0.912 and -0.907 eV for boron, carbon, and nitrogen respectively, suggesting more stability when attached via boron atom. As a result, the optimized structural geometries of various EWG and EDG groups on PPPh-functionalized sheets are illustrated in **Figure 4.2**.

The calculated average B-N, B-C, N-C, and C=C bond distances in pristine BCNNS are 1.45, 1.51, 1.40, and 1.39 Å, respectively. These values are consistent with previously reported experimental [206,207] values, validating the computational methods employed in this study. Upon functionalization with PPPh, no significant changes were observed in these bond lengths. Similarly, further functionalization of PPPh with various electron-withdrawing (EWG) and electron-donating groups (EDG) results in no significant changes

in B-N, B-C, and C=C bond distances in the nanosheet. However, a slight decrease in N-C bond length was observed in the case of functionalization with the Amine and methyl groups. This can be explained on the basis of the electron-donating effect of these groups, which increases the electron density in the polymer chain, causing a partial transfer of electrons to the BCN nanosheet, thereby weakening the N-C bonds and reducing their bond lengths. Furthermore, in the case of $M/M^{n+}@BCNNS$ complexes, the B-N, B-C, N-C, and C=C bond distances remain relatively unchanged, except for $Mg^{2+}@BCNNS$, where a slight decrease in N-C bond length was observed. This is likely due to the Mg^{2+} larger ionic radius and higher charge density, enabling stronger electrostatic interactions and polarization of the N-C bonds, leading to a weakening and contraction of these bonds (**Table 4.1**). The findings demonstrate the stability and substantial impact of functional group changes on the structural and electrical characteristics of PPh-BCNNS complexes.

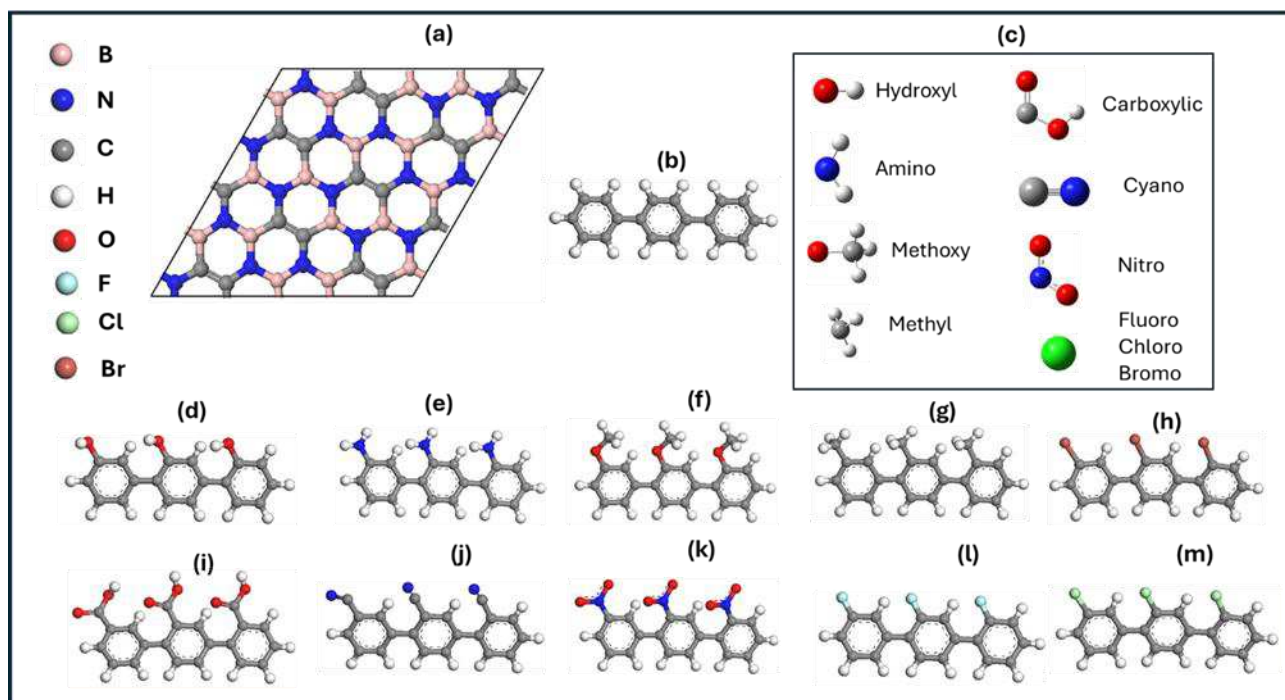


Figure 4.1 Optimized geometries of (a) pristine boron nitride nanosheet (BCNNS), (b) repeat unit of the poly-p-phenylene (PPPh), (c) selected electron withdrawing and electron donating groups (EWG & EDG), (d) hydroxy@PPPh, (e) amino@PPPh, (f) methoxy@PPPh, (g) methyl@PPPh, (h) bromo@PPPh, (i) carboxyl@PPPh, (j) cyano@PPPh, (k) nitro@PPPh, (l) fluoro@PPPh, and (m) chloro@PPPh.

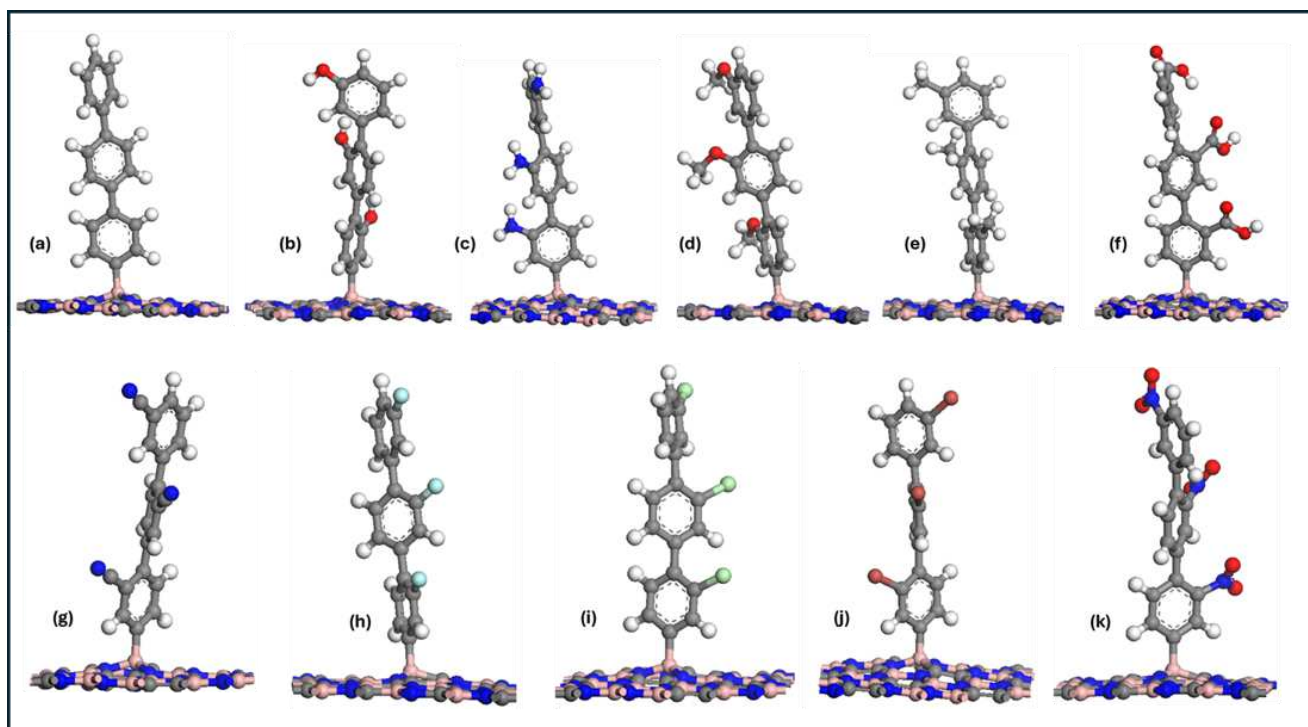


Figure 4.2 Optimized geometries of (a) PPPh-BCNNS, (b) hydroxy@PPPh-BCNNS, (c) amino@PPPh-BCNNS, (d) methoxy@PPPh-BCNNS, (e) methyl@PPPh-BCNNS, (f) carboxyl@PPPh-BCNNS, (g) cyano@PPPh-BCNNS, (h) nitro@PPPh-BCNNS, (i) fluoro@PPPh-BCNNS, (j) chloro@PPPh-BCNNS, (k) bromo@PPPh-BCNNS.

Table 4.1 Calculated boron to nitrogen bond distance in BNNS and adsorption distances of metal and metal-ion on bare BNNS and PPh-BNNS complex

Complex	Bond distance (Å)						
	B-N	B-C	C-N	C-C	M-B	M-N	M-C
Li@BCNNS	1.44	1.52	1.41	1.40	2.32	2.23	2.26
Li⁺@BCNNS	1.44	1.51	1.40	1.40	2.32	2.23	2.26
Na@BCNNS	1.44	1.52	1.40	1.39	2.67	2.61	2.64
Na⁺@BCNNS	1.44	1.50	1.40	1.40	2.64	2.60	2.62
Be@BCNNS	1.45	1.52	1.40	1.38	2.18	1.81	1.86
Be²⁺@BCNNS	1.42	1.52	1.39	1.40	2.09	1.77	1.82
Mg@BCNNS	1.45	1.51	1.39	1.40	3.10	3.41	2.97
Mg²⁺@BCNNS	1.45	1.51	1.37	1.39	2.72	2.95	2.57
Li@PPPh-BCNNS	1.43	1.51	1.40	1.40	2.52	2.90	2.16
Li⁺@PPPh-BCNNS	1.42	1.50	1.37	1.40	2.92	2.80	2.41
Na@PPPh-BCNNS	1.43	1.50	1.39	1.40	3.59	2.72	2.51
Na⁺@PPPh-BCNNS	1.45	1.52	1.39	1.40	2.99	3.62	3.14
Be@PPPh-BCNNS	1.44	1.51	1.39	1.39	2.08	1.70	1.75
Be²⁺@PPPh-BCNNS	1.43	1.49	1.39	1.39	2.03	1.84	1.89
Mg@PPPh-BCNNS	1.42	1.51	1.37	1.42	2.81	3.28	2.33
Mg²⁺@PPPh-BCNNS	1.45	1.52	1.382	1.41	2.94	2.98	2.26

4.3.2 Impact of functionalization on BCNNS.

2D boron nitride reportedly has a wide band gap of about 5 eV due to the significant differences in the electronegativity between boron and nitrogen atoms leading to a polarized electronic structure, resulting in a wide bandgap [208]. However, the boron carbon nitride BCN nanosheet has been reported to have a bandgap of around ~0 eV, which is attributed to the incorporation of carbon atoms into the BN lattice [258-259]. Carbon atoms introduce mid-gap states, which narrow the bandgap, and in some cases, even lead to the formation of a Dirac cone, similar to graphene, resulting in a semi-metallic or metallic behavior with a zero or near-zero bandgap [209]. While our calculated band gap agrees with the above statements, this could have undesirable effects on metal ion battery applications. These effects could span from uncontrolled electron transfer, increased electrical conductivity, reduced ion diffusion, increased risk of electrode degradation, and safety concerns, ultimately leading to reduced battery performance, lifespan, and reliability [210]. The functionalization of BCNNS with PPPh conducting polymers and consequently various electron-withdrawing and electron-donating groups incredibly tuned the electronic properties of the BCNNS. The calculated band gap for the complexes ranges from 0.14 to 0.36 eV across the PPPh functionalized with various EWG and EDG. These values represent an increase in the band gaps with the PPPh, carboxy-PPPh, cyanide-PPPh, chloro-PPPh, and bromo-PPPh functionalized BCNNS having the highest and lowest percentage increase of 36, 35 and 36, and 14 % respectively as depicted in **Figure 4.3**.

Generally, functionalization with PPPh and PPPh functionalized with various EDG and EWG increase the bandgap, thereby improving the electronic properties of the BCN nanosheet. However, functionalization with Bromo-PPPh is more desirable for ion battery

applications as it introduces a smaller increase in the bandgap of 14 % that could be in the range for efficient charge carrier mobility and ion diffusion. In contrast, the larger bandgap introduced by functionalization with PPPh, carboxy-PPPh, cyanide-PPPh, and chloro-PPPh may lead to reduced charge carrier mobility and increased electron-hole recombination, ultimately compromising the battery's performance and efficiency. Furthermore, the bromo- group functionalized on PPPh could enhance the material's electrochemical properties by improving redox activity, metal ion binding, conductivity, and stabilization of metal ions, making it a promising candidate for metal-ion battery applications. This could be achieved through a synergistic mechanism involving electron-withdrawing effects, redox mediation, conductivity enhancement, and metal ion stabilization, thereby facilitating efficient charge transfer and ion uptake.

The findings underscore the substantial influence of functional groups, especially the Bromo group, on the electrical and structural characteristics of PPPh-BCNNS complexes. Following these discoveries, adsorption investigations were performed on Bromo-functionalized PPPh-BNNS complexes with different metals and ions, as depicted in **Figure 4.4**.

In addition, global reactivity descriptors such as electronegativity and electrophilicity (ω) were employed to assess the effects of functionalization on BCNNS. Electronegativity is a measure of an atom's ability to attract and hold onto shared electrons in a covalent bond, with higher electronegativity values indicating a greater tendency to pull electrons towards itself. In metal-ion batteries, the electronegativity of the electrode material influences metal ion binding, mobility, and charge transfer, with higher electronegativity values enhancing ionic interactions and electrochemical performance. The electrophilicity index (ω),

established by Parr et al. [166], is based on chemical potential and hardness. This index quantifies the energy decrease linked to optimum electron transport between donor and acceptor species, offering insights into the system's reactivity and stability. A higher electrophilicity index indicates a stronger tendency to attract electrons, which can enhance the system's reactivity and interaction with other species, such as metal ions in a battery. As shown in **Figures 4.5 and 4.6**, Bromo-PPPh functionalized BCNNS exhibited the highest values of electronegativity and electrophilicity. The incorporation of bromine functional groups into PPPh conducting polymers significantly enhances the electronic properties of BCNNS, as evidenced by an elevated electrophilicity index (ω) and electronegativity. This modification facilitates efficient charge transfer, augments conductivity, and strengthens ion interactions, ultimately yielding improved cell voltage, capacity, and overall electrochemical performance in metal-ion batteries. These findings underscore the potential of Bromine as a functional group for optimizing the electrochemical properties of the PPPh-BCNNS complex, rendering them promising candidates for advanced energy storage applications.

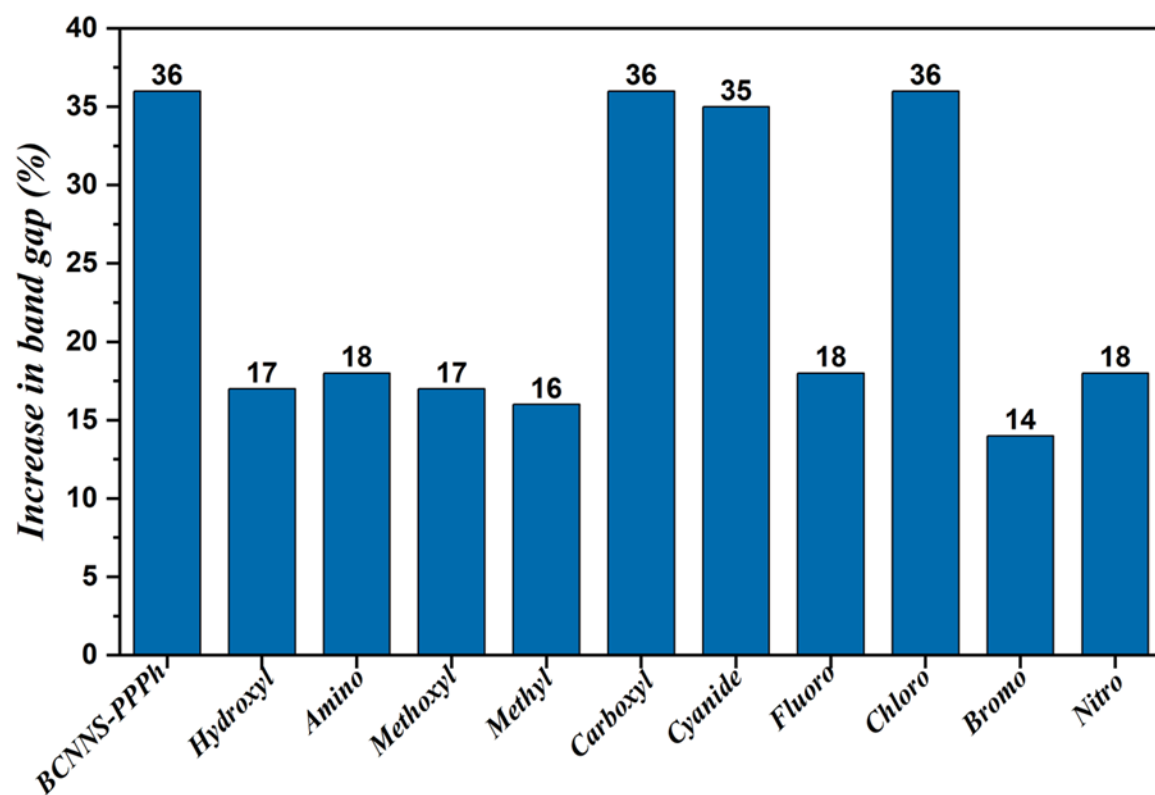


Figure 4.3 Calculated percentage Increase in band gap of PPh-BCNNS, and various electron-withdrawing and electron-donating groups functionalized on PPh-BCNNS complexes.

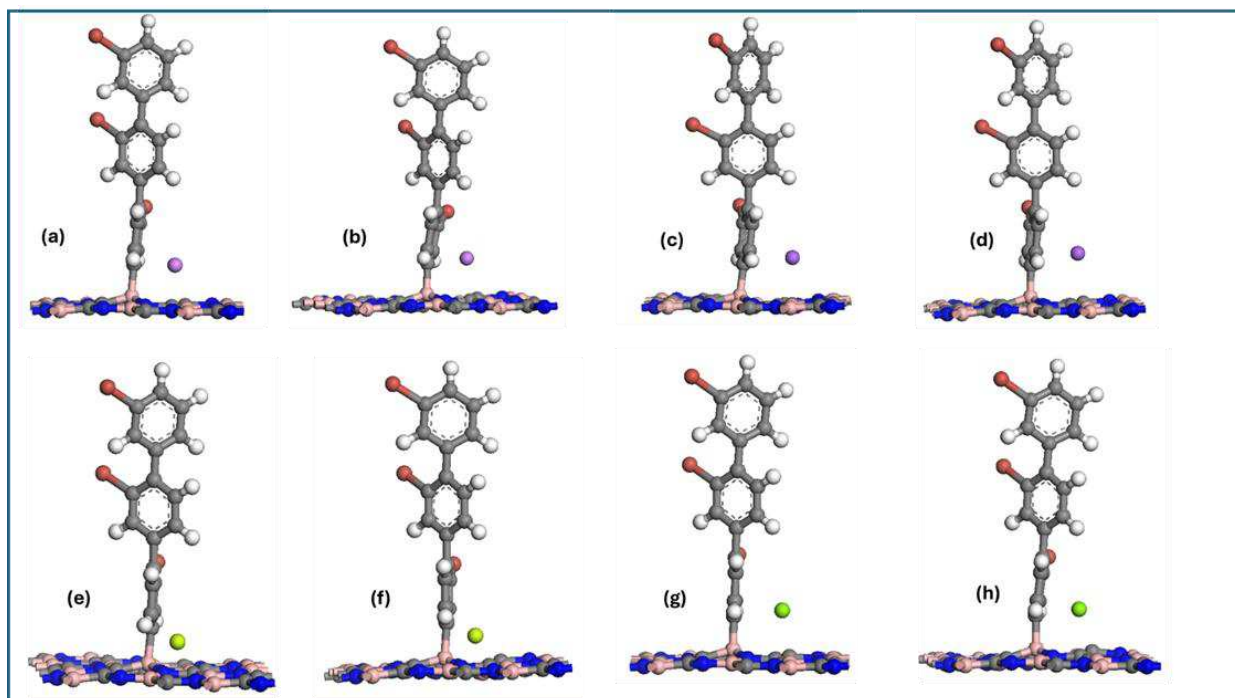


Figure 4.4 Optimized adsorption structures of various metals/ions on the potential Bromo-group functionalized PPPh-BCNNS complex namely (a) Li@PPPh-BCNNS, (b) Li^+ @PPPh-BCNNS, (c) Na@PPPh-BCNNS, (d) Na^+ @PPPh-BCNNS, (e) Be@PPPh-BCNNS, (f) Be^{2+} @PPPh-BCNNS, (g) Mg@PPPh-BCNNS, (h) Mg^{2+} @PPPh-BCNNS complexes.

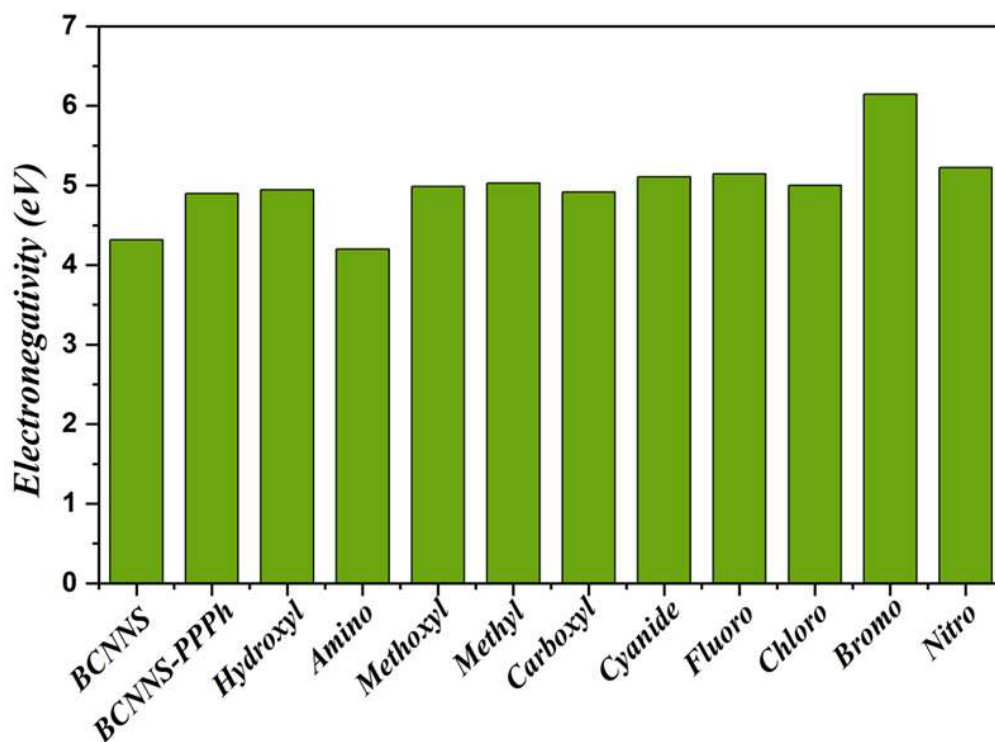


Figure 4.5 Calculated electronegativity of BCNNS, PPh-BCNNS and PPh-BCNNS functionalized with various EWG and EDG.

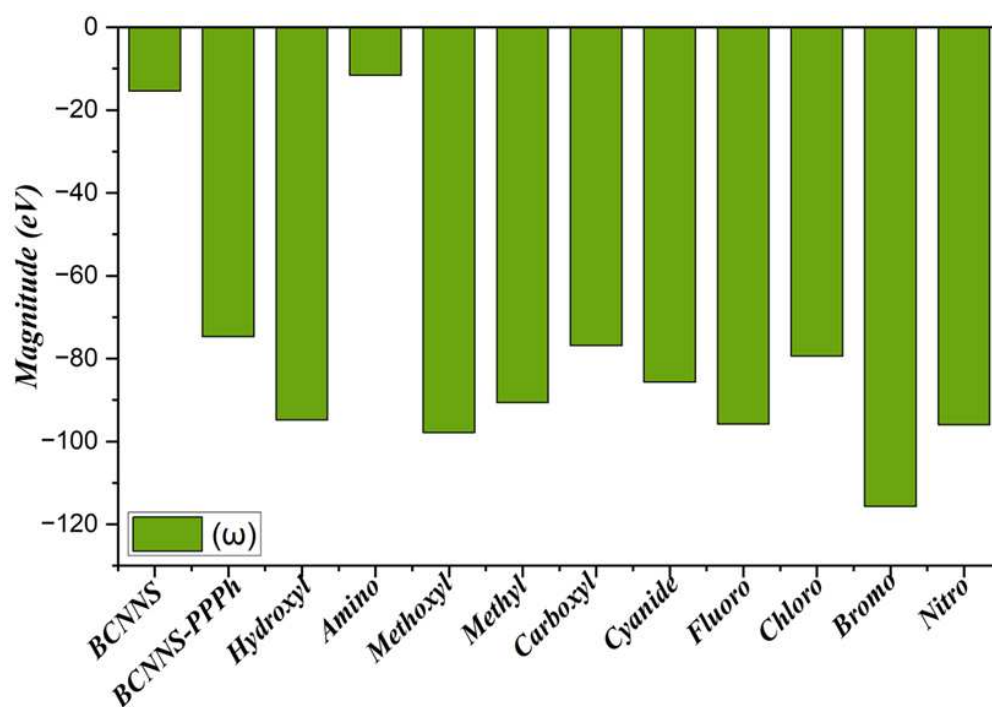


Figure 4.6 Estimated electrophilicity of BCNNS, PPh-BCNNS and PPh-BCNNS functionalized with various EWG and EDG.

4.3.3 Adsorption of Li/Li⁺, Na/Na⁺, Be/Be²⁺ and Mg/Mg²⁺ on BCNNS and PPPh-BCNNS

Haven previously discussed the impact of various metals/ions on the electronic structure and properties of bare BCNNS. Here, we summarize the nature of adsorption, focusing on the metal/ion-boron, metal/ion-nitrogen, and metal/ion-carbon bond distances for different M/Mⁿ⁺ species on pristine BCNNS and the bromo-group functionalized PPPh-BCNNS as shown in **Table 1**. On the adsorption of M@BCNNS, the bond distances between the metal atom and the nanosheet range from 1.81 to 3.41 Å, with the Be@BCNNS exhibiting the shortest bond distances (**Fig. 4.7**). This might be due to its smaller atomic radius and highest electronegativity value of Be resulting in stronger electrostatic attraction and covalent interaction with the nanosheet, thereby minimizing the adsorption distance. Similarly, no significant changes were observed in bond distances in the case of M⁺@BCNNS when compared to the metals with the exception of Mg²⁺@BCNNS which undergoes a shorter bond length when compared to the Mg@BCNNS metal counterpart. This can be attributed to the higher effective nuclear charge (Z_{eff}) and smallest ionic radius when compared to Li⁺, Na⁺, and Be²⁺ resulting in a stronger electrostatic attraction to the negatively charged BCN nanosheet, thereby minimizing the adsorption distance.

Upon functionalization with bromo-PPPh, these bond distances remain relatively unchanged. This can be attributed to the fact that the bromo-PPPh conducting polymer primarily interacts with the BCNNS through π - π stacking and van der Waals forces, without significantly altering the electrostatic and covalent interactions between the metal atoms/ions and the nanosheet. As a result, the adsorption distances remain relatively unchanged. Furthermore, this indicates a high degree of stability in the complex.

Suggesting that the interaction between the metal atoms/ions and the BCNNS is robust and resistant to perturbations, such as the introduction of the bromo-PPP polymer. Such stability is crucial for maintaining electrochemical performance and durability of the complex in applications such as energy storage and conversion.

Additionally, the ΔE_{cell} and cell voltages generated by the adsorption of M/M^{n+} on BCNNS and bromo-PPPh-BCNNS are shown in **Figures 4.9a&b**. Adsorption energies, essential for optimizing metal-ion battery performance, were evaluated. Elevated adsorption energy values indicate enhanced stability of the material during electrochemical reactions [211]. An increase in adsorption energies was observed upon functionalization with bromo-PPPh when compared to the pristine nanosheet. It is also worth noting that in the case of monovalent species, the $M@$ bromo-PPPh-BCNNS exhibit higher adsorption energies than the corresponding $M^+@$ bromo-PPPh-BCNNS, however, in the case of divalent species the ionic counterparts exhibit higher adsorption energies. The observed trend in adsorption energies can be attributed to the fact that the monovalent metal atoms (Li and Na) exhibit stronger covalent interactions with the PPPh functionalized BCNNS due to their lower ionization energies, whereas the divalent ions (Be^{2+} and Mg^{2+}) exhibit stronger electrostatic attractions to the nanosheet due to their higher charge density. Generally, these findings suggest that bromo-PPPh functionalization enhances metal/ion mobility and system stability.

In addition, the diffusion characteristics of various metal ions across the sheet were investigated. The plot of mean square deviation versus the time steps showing the diffusion patterns across the sheet is illustrated in **Figure 4.8**. Different diffusion patterns were

observed in the PPh-BCNNS across the metal ions. For instance, Na^+ and Mg^{2+} show a more linearity in their diffusion pathway and exhibit higher diffusion coefficient values of 5.5 and 3.28 cm^2/s respectively. On the other hand, Li^+ and Be^{2+} show non-linearity in their diffusion pattern and exhibit lower diffusion coefficient values of 0.73 and 0.15 cm^2/s . The higher diffusion coefficients and linear diffusion behavior exhibited by Na^+ and Mg^{2+} across the PPh-BCNNS might be due can be attributed to the relatively larger ionic radius and lower charge density, resulting in weaker interactions with the functionalized 2D boron carbon nitride nanosheet. While the observed non-linear diffusion patterns of Li and Be ions are likely due to their stronger electrostatic interactions and specific binding sites with the functionalized nanosheet.

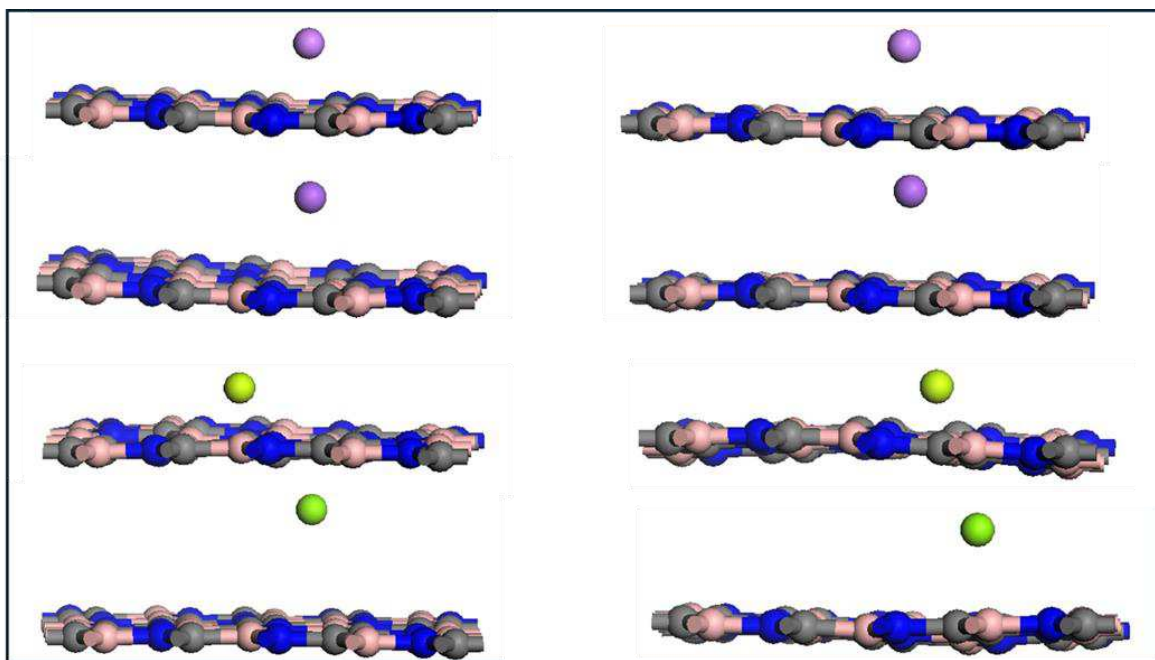


Figure 4.7 Cross-sectional view of Optimized structures of (a) Li@BCNNS, (b) Li⁺@BCNNS, (c) Na@BCNNS, (d) Na⁺@BCNNS, (e) Be@BCNNS, (f) Be²⁺@BCNNS, (g) Mg@BCNNS, (h)Mg²⁺@BCNNS.

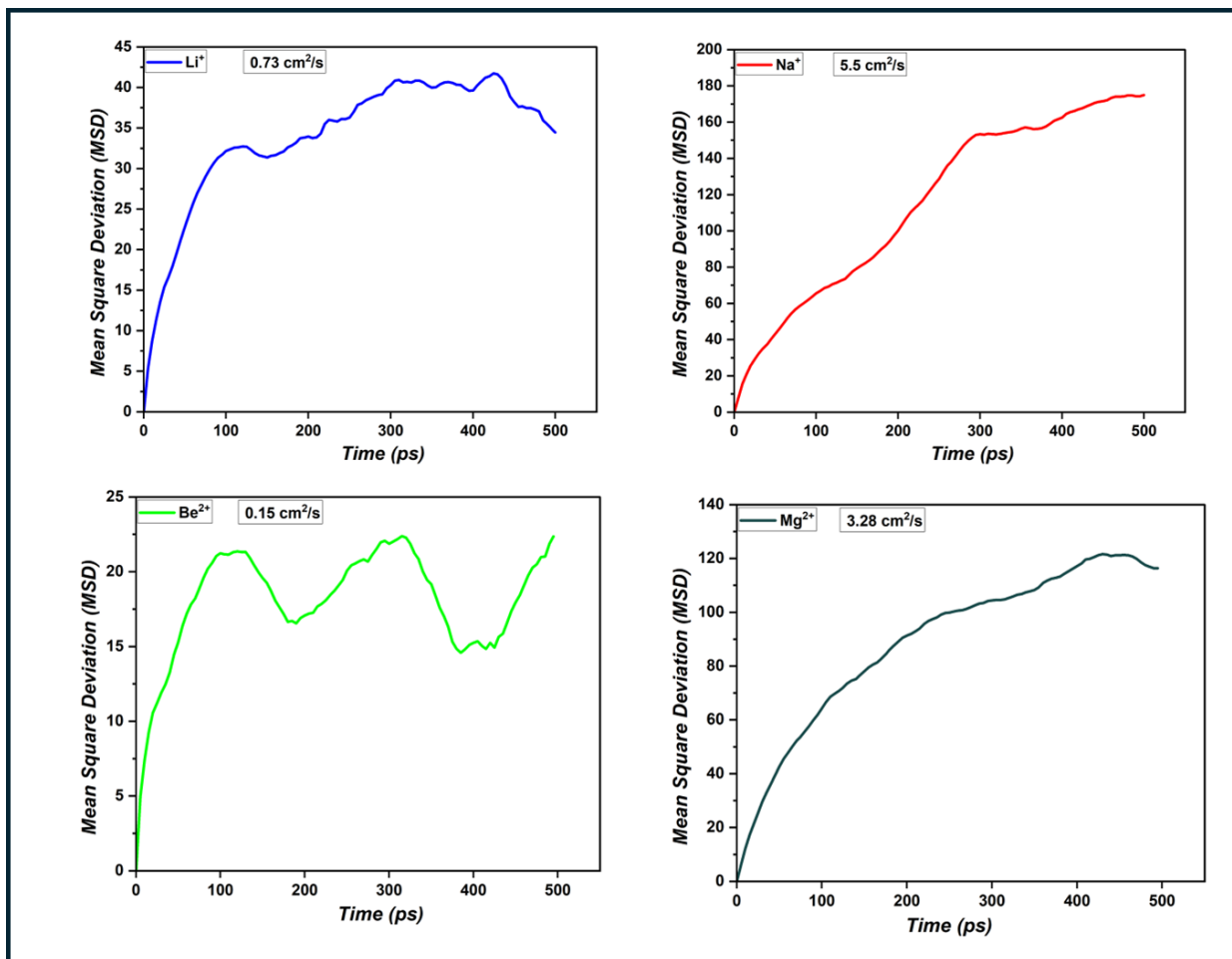
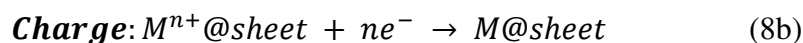
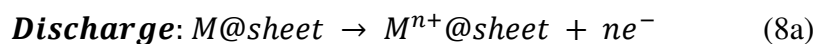
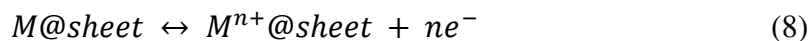


Figure 4.8 Diffusion pattern of various metal ions across the nanosheet

4.3.4 Ion battery Application of BCNNS and bromo-PPPh-BCNNS

BCNNS and bromo-PPPh-BCNNS function as anode materials for ion batteries. The electrochemical processes at the anode and cathode half-cells are outlined in Equations 8 and 9, aligning with previous studies [140,169,175]. The corresponding overall cell reaction is summarized below.

At anode:



At cathode:



Overall cell reaction:



Where M, M^{n+} , and sheet denote the metal atoms, the metal ions, and the BCNNS and/or bromo-PPPh-BNNS, respectively

Figure 4.9 present the adsorption energies metal/ions on BCNNS and bromo-PPPh functionalized sheets. The relative increase in adsorption energy upon functionalization indicates the improved stability of the complex materials enhanced electron diffusion, and

extended cycle life [212]. This underscores the critical role of the nitro-PPPh functionalized substrate in improving metal/ion interactions and increasing cell voltages.

As shown in **Figure 4.10**, the calculated cell voltages for $M/M^{n+}@BCNNS$ and $M/M^{n+}@bromo-PPPh-BCNNS$ systems are influenced by the charge density and size of the adsorbed metal atoms or ions. For example, it shows observed that the cell voltage decreases generally down the group with $Li@BNNS$, $Na@BNNS$, $Be@BCNNS$, and $Mg@BCNNS$ having the cell voltage values of 1.05, 0.84, 5.94, and 4.24 V respectively. Furthermore, upon functionalization with bromo-PPPh, there was an increase in the cell value with values of 2.62, 2.59, 8.20, and 6.02 eV for the designed LIBs, SIBs BIBs, and MIBs respectively. This trend can be attributed to the decrease in ionization energies, resulting from the increase in atomic radius and decrease in electronegativity, which facilitates easier ionization and reduction, thereby lowering the overall cell voltage. Generally, the designed alkaline earth metal batteries exhibit higher cell voltage than the alkali metal batteries.

Overall, incorporating bromo-PPPh with BCNNS notably enhances its electrochemical properties. This functionalization tunes the band gap between conduction and valence bands, boosts conductivity, expands the electroactive surface area, and reduces interfacial resistance. These advancements promote improved reversibility of metal-ion reactions at the electrodes, yielding superior battery performance, accelerated charge/discharge rates, and a prolonged lifespan [140].

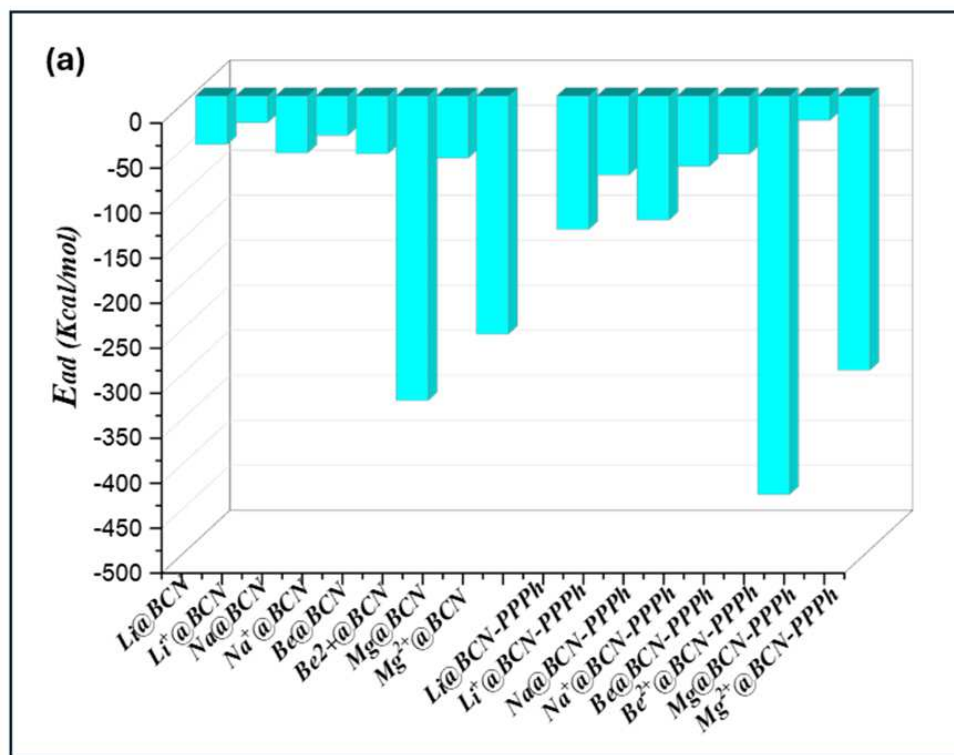


Figure 4.9 Depicts the calculated cell energies (ΔE_{cell}) of M/Mn+@BNNS and M/Mn+@PPh-BCNNS.

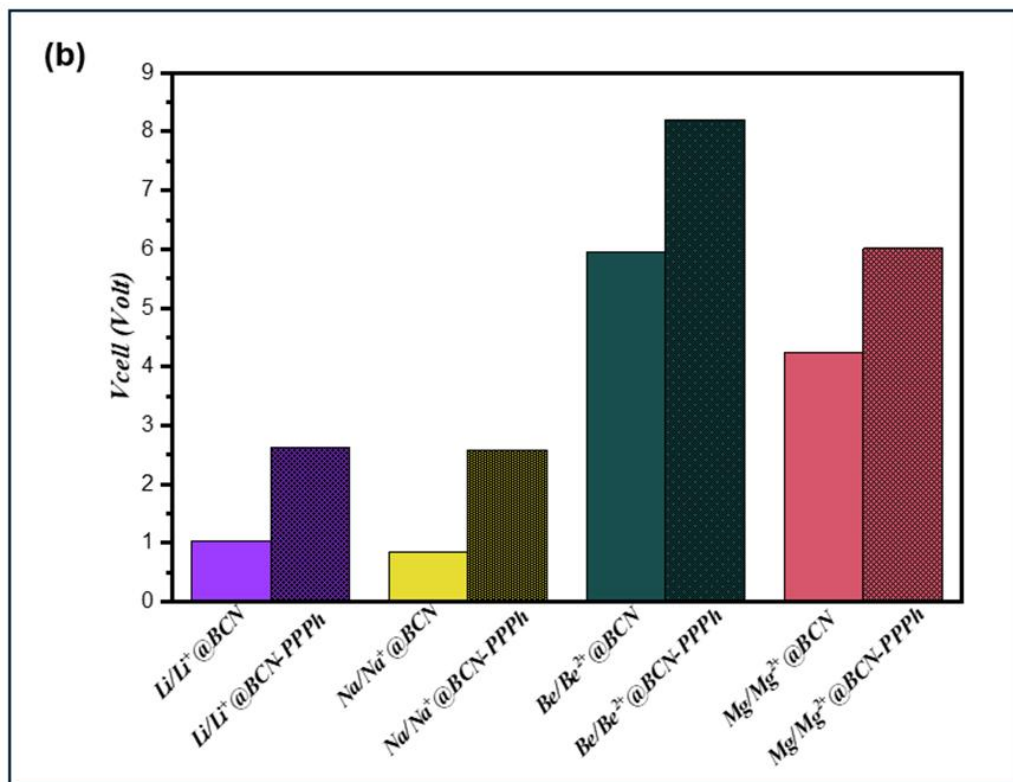


Figure 4.10 The calculated cell voltages of M/Mn+@BNNS and M/Mn+@PPPh-BCNNS.

4.3.5 Thermal stability.

A pivotal factor in determining a material's suitability for high-temperature environments is its capacity to retain structural stability under defined thermal conditions. High temperatures, often generated by internal battery reactions, can deform electrode materials, shortening battery longevity. Consequently, evaluating the thermal stability of electrode components is critical. This study utilized dynamic simulations to assess the thermal behaviour of BCNNS and bromo-PPPh-BCNNS, as illustrated in **Figure 4.10**.

The simulations employed a $5 \times 5 \times 1$ supercell model, using 0.5 fs time steps over 2000 iterations, resulting in a total simulation time of 1 ps conducted at 300 K and 500 K. Slight fluctuations in potential energy were observed at 300 K as well as 500 K, however, the structural integrity of the pristine BCNNS remains intact. Following functionalization with bromo-PPPh, a significant reduction in fluctuations and stable potential energy was observed at both 300 K and 500 K.

This enhanced stability can be attributed to the strong π - π stacking interactions and covalent bonding between the Bromo-PPPh CP and the BCNNS, which leads to a more rigid and stable structure. This interaction further enhances thermal stability by reducing molecular motion and fluctuations in potential energy. These findings indicate that functionalized BCNNS exhibits improved thermal stability, making it a promising anodic material for high-temperature applications. These findings indicate that functionalized BCNNS exhibits improved thermal stability, making it a promising anodic material for high-temperature applications.

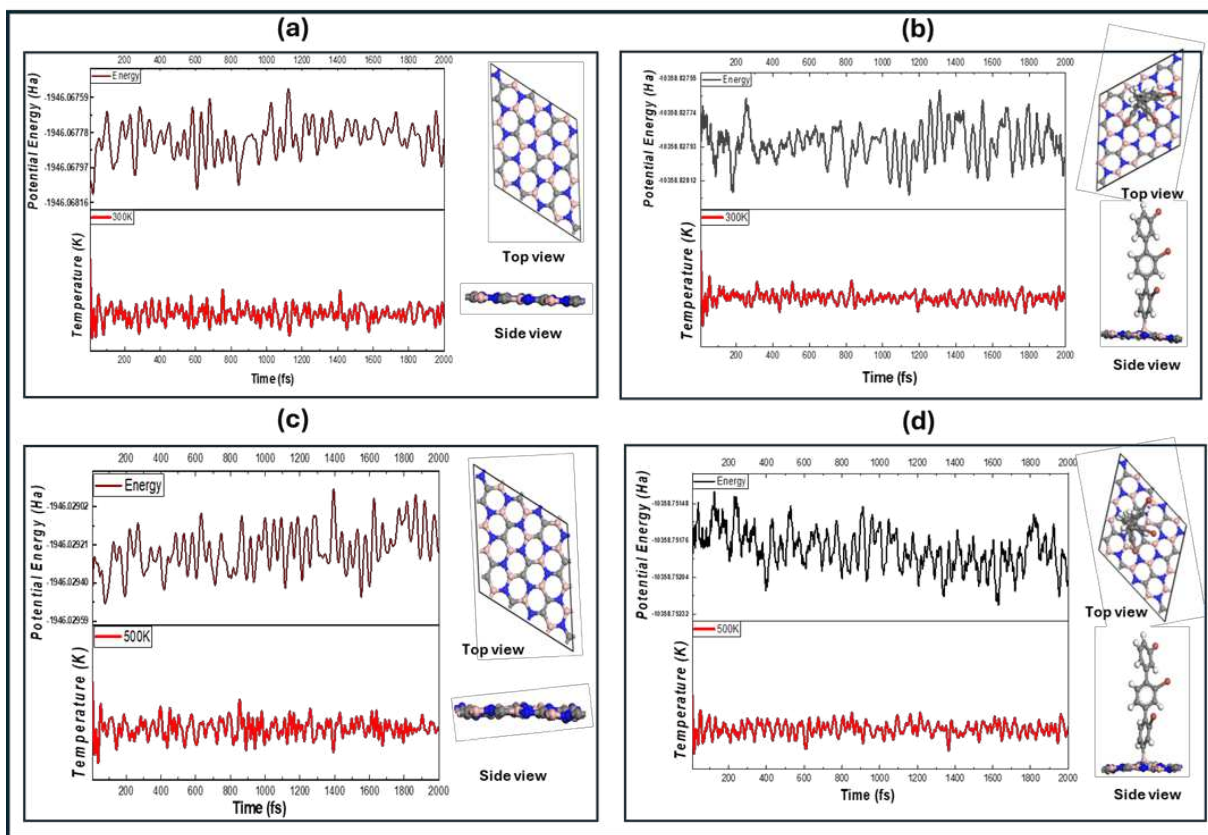


Figure 4.11 The simulated dynamics temperature and potential energy fluctuations with the corresponding final geometrical structures of (a) bare BCNNS 300k, (b) PPh-BCNNS @300K, (c) bare BCNNS @500k and (d) PPh-BCNNS @500k

4.3.6 Open circuit voltage and theoretical specific capacity

The open circuit voltage (OCV) is a crucial parameter for assessing the performance of metal ion batteries, offering valuable information about the thermodynamic properties and electrochemical characteristics of battery materials. In this study, we expand our research to estimate the theoretical capacity and average open circuit voltage of lithium-ion batteries (LIB) and sodium-ion batteries (NIB), which are among the most well-developed metal ion battery technologies. OCV is often calculated from the Nernst equation ($\frac{-\Delta G}{zF}$). However, since the entropy, and volume effect are considered negligible at room temperature [177], the OCV can be estimated from the differences in adsorption energies of the metals using the equation below [178]:

$$\text{OCV} = \frac{-[EM_x\text{PPPh/BCNNS} - (x-x_0)EM - ELi_{x_0}\text{PPPh/BCNNS}]}{(x-x_0)} \quad (11)$$

Where PPPh/BCNNS , EM is and $(x - x_0)$ represent the bromo-PPPh functionalized BCNNS, the energy of an isolated metal atom, and the number of metal atoms taking part in the reaction per unit formula respectively. Similarly, to establish the OCV profile, the formation energies were used to investigate the stabilities of the intermediate structures through the injection of 1 to 10 metal atoms **Fig.4.12**. Thus, the formation energies of the intermediate structures were estimated using the equation below:

$$E_{if} = EM_{x\text{sheet/poly}} - \frac{(xEM_{10}\text{PPPh/BCNNS} + (10-x)E\text{PPPh/BCNNS})}{10} \quad (12)$$

Where E_{if} and x are the intermediate formation energy and the number of substituted metal atoms respectively.

The convex hull plot for the intermediate phase formation is illustrated in **Figures 4.13** and **4.14**. For the $\text{Li}_x\text{BCNNS-PPPh}$ system, one intermediate phase at $x = 9$ was identified as thermodynamically unstable. However, three unstable intermediate phases were identified for the $\text{Na}_x\text{BCNNS-PPPh}$ at $x = 4, 5$, and 8 . Since metal interaction calculations are based solely on phases lying on the convex hull, these unstable intermediate structures were excluded from further analysis [45]. The open-circuit voltage (OCV) profile is depicted in **Figure 4.15c-d**. During the lithiation process, a significant voltage drop was observed, decreasing from 3.60 V at $x = 1$ to 2.78 V at $x = 3$, followed by sequence decrease in voltage. Similarly, in the sodiation process, a sharp reduction in voltage was recorded, from 3.17 V at $x = 1$ to 2.56 V at $x = 2$. The significant voltage drops observed can be linked to increased electrostatic interactions between the metal ions and the BCNNS framework. In general, the open-circuit voltage (OCV) profile shows a declining trend as more metal atoms are intercalated. At a certain concentration of metal ions, the discharge voltage levels off, signalling the system's peak energy storage capability. The computed average OCVs for the designed lithium-ion battery (LIB) and sodium-ion battery (SIB) systems are 2.47 V and 1.96 V , respectively, exceeding the reported values for previously investigated materials.

The theoretical specific capacity is a fundamental metric for evaluating the electrochemical performance of electrode materials, as it measures the energy storage potential per unit mass. It is generally determined using the following formula [177]:

$$C_m = \frac{xF}{M}$$

Where C_m is the specific capacity, x is the number of electrons involved in the electrochemical process, F is the Faraday constant and M is the molar mass of bromo-PPPh-BCNNS.

The estimated maximum specific capacities for the designed lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) are 248 mAh/g and 223 mAh/g, respectively. Although these values are lower than those of commercial graphene [178], they surpass the specific capacities reported for MoS₂ [180] and MoC₂ [181]. This suggests that BCNNS-functionalized PPPh-based electrodes demonstrate encouraging electrochemical properties, especially for high-voltage applications that demand stable and efficient energy storage.

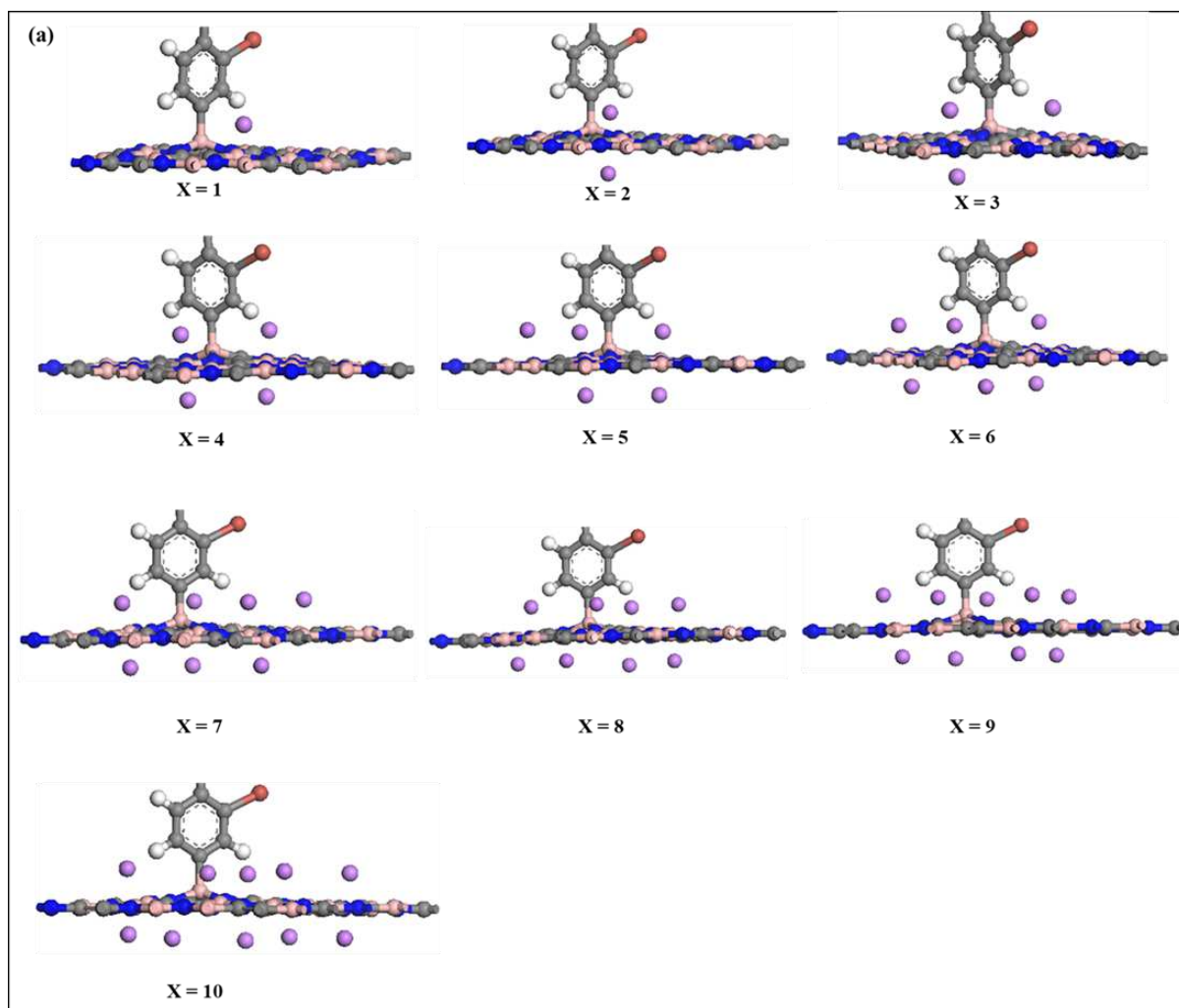


Figure 4.12 Configurations of $\text{Li}_x\text{BCNNS-PPPh}$ with Li binded on both sides of the boron carbon nitride nanosheet.

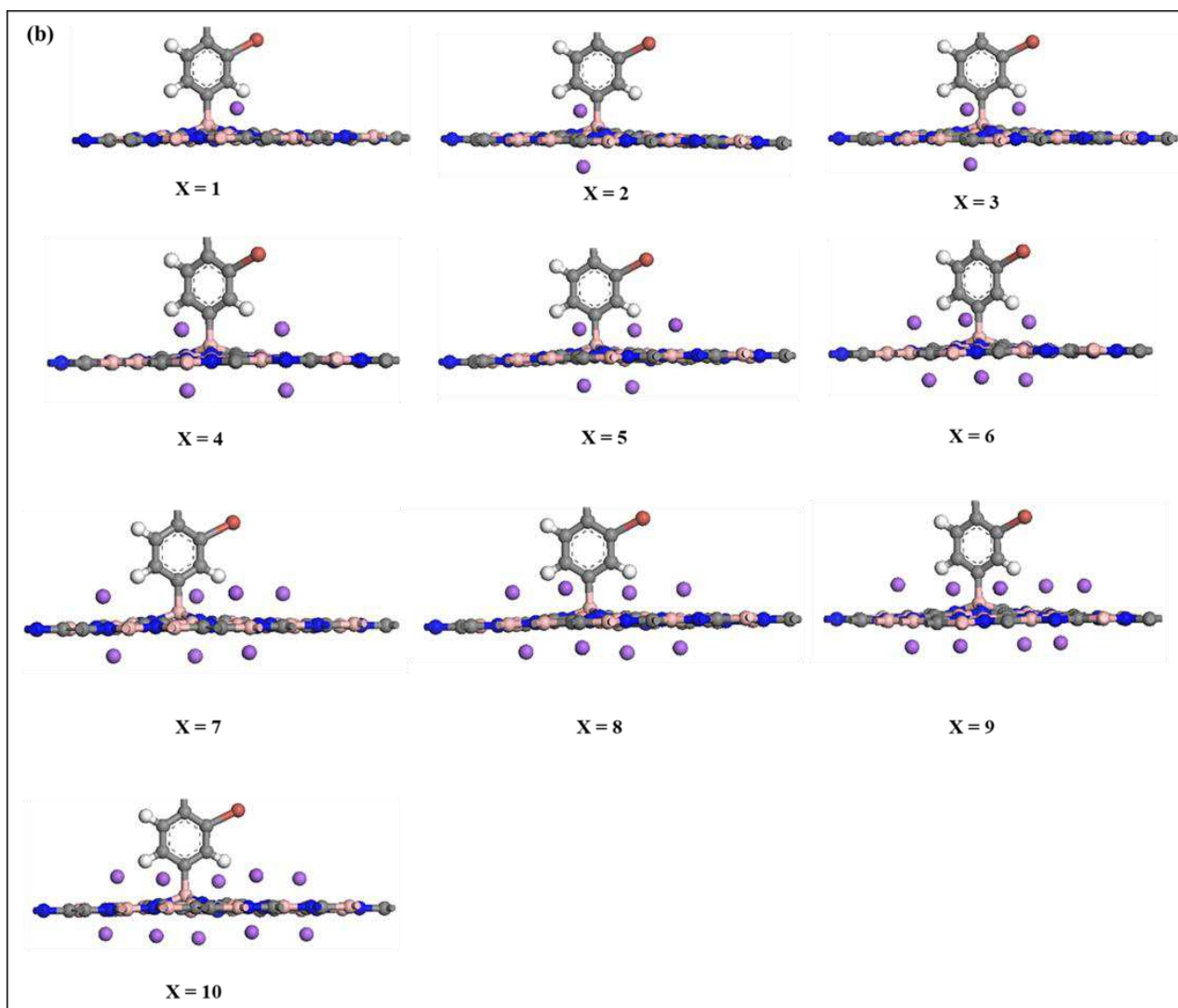


Figure 4.13 Configurations of $\text{Na}_x\text{BCNNS-PPPh}$ with Na binded on both side of the boron carbon nitride nanosheet.

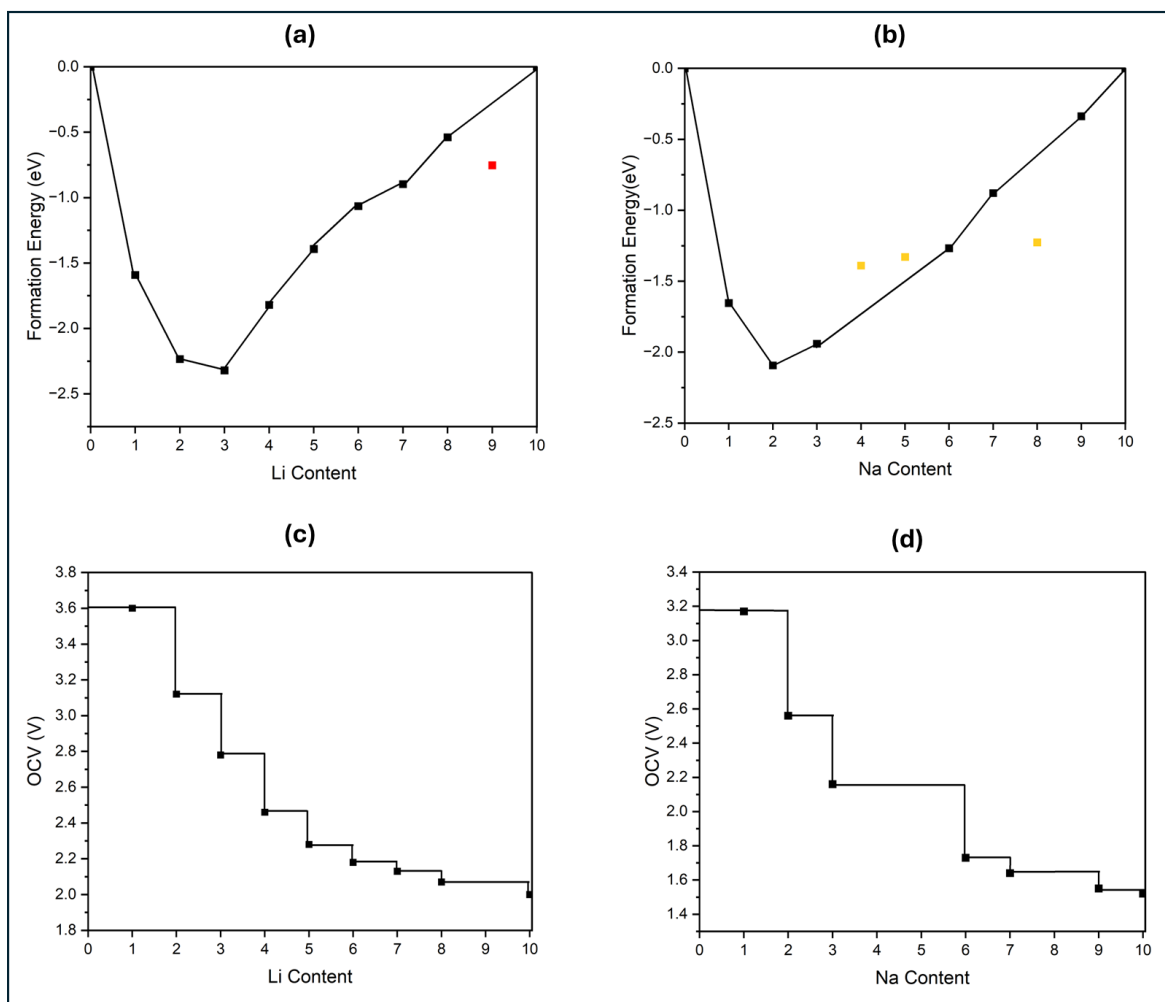


Figure 4.14 The intermediate formation energies of (a) $\text{Li}_x\text{BCNNS-PPPh}$ (b) $\text{Na}_x\text{BCNNS-PPPh}$, and the corresponding voltage profile of (c) $\text{Li}_x\text{BCNNS-PPPh}$ and (d) $\text{Na}_x\text{BCNNS-PPPh}$, with respect to Li and Na content from 0 to 10.

CHAPTER 5

ENGINEERING ANODIC MATERIALS FOR METAL-ION BATTERIES WITH CONDUCTING POLYMER FUNCTIONALIZED BORON NITRIDE NANOCAGES: A DFT PERSPECTIVE

5.1 Introduction

In recent decades, second-generation batteries have garnered considerable attention for their promise of being the most feasible energy storage solution for diverse applications, including electric motor vehicles and portable electronic gadgets [213-215]. During charging and discharging cycles, they enable the transfer of metal ions between the anode and cathode. A typical alkali ion battery usually comprises two electrodes which are divided by a conductive electrolyte with the ions functioning as electrolytic cells. During the charging phase, the ions move under the influence of applied external force. Thus, fulfilling a certain magnitude of voltage or current requires multiple interconnected electrochemical cells [216-218]. The properties of the electrode material dictate the overall energy storage and discharge capabilities of the cell. Despite the considerable progress in the creation of Li-ion batteries (LIBs), numerous challenges are encountered, including inadequate safety, restricted lifespan, low operational temperature, and elevated cost [219-220]. The rising demand for LIBs as energy storage systems, coupled with limited lithium resources, has driven up the pricing of devices utilizing these batteries, hence encouraging researchers to explore alternative ion batteries. Sodium-ion batteries (SIBs) could constitute a feasible substitute for LIBs in the near future owing to their non-toxicity, abundance, and cost efficiency [221]. Despite their benefits, SIBs have been documented to exhibit diminished energy and power density, electrode degradation, and significant volumetric expansion [222-223]. Consequently, it is increasingly apparent that the

intelligent molecular engineering of electrode materials, taking into account the electronic characteristics, chemical functionalities, and thermodynamic properties of active materials, can significantly influence the electrochemical performance, power output, and energy density of metal-ion batteries [224-225].

To achieve further advancements, researchers have redirected their attention to fullerenes and nanocages as a main framework for the anodic material fabrication. Scientific investigations indicate that the electrode electrochemical performance and charge storage capacity can be improved through structural alterations, including atomic doping and functionalization [226]. Xiaoxia et al. [227] produced an inorganic fullerene-like molybdenum sulfide (IF-MoS₂) nanocage featuring a hollow structure, which was assessed as an anode material for LIBs. The research indicated that the nanocage offers substantial expandable volumes for alterations during cycles and concluded that this highly sought-after structure can markedly improve lithium storage performance, evidenced by the increased reversible capacity, exceptional cycling behavior, and superior rate capability. Furthermore, Changsheng et al. [228] studied the functionalization of spherical C₆₀ derivatives with carboxyl and ester groups which is proposed as an anodic material in LIBs. The research reported an enhanced high-charge capacity of 861 mAhg⁻¹ for carboxyl functionalized-C₆₀. Theoretical studies have been employed to evaluate the feasibility of different fullerenes and nanocages as electrode materials for secondary batteries. For instance, Rong-Jun et al through density functional theory (DFT) simulations examined the electrochemical properties of F-doped Si₁₉Ge₁₉ as an anodic electrode for the designed K-ion batteries and attaining a cell voltage of 2.2 V [229-230]. Jianfeng and colleagues conducted a theoretical investigation of carbon and germanium nanocages as anode

electrodes in Na-ion and K-ion batteries, achieving voltages of 1.78 V for $\text{Na}^+\text{-C}_{48}$ and 1.19 V for $\text{K}^+\text{-Ge}_{48}$. [231]. Also, Duraisamy et al studied the influence of halide (F^- , Cl^- , and Br^-) encapsulation in $\text{Be}_{12}\text{O}_{12}$ nanocages analyzed as an electrode material for K-ion, Na-ion, and Li-ion batteries. The findings indicated an enhancement in cell voltage following the encapsulation of F^- ions resulting in a notable increase of 3.23 V for LIBs [232]. The improvement in the efficiency of lithium-ion battery technology depends on the continuous development of new generations of electrode nanomaterials. Recent research on Li-ion batteries has concentrated on anodic materials demonstrating elevated reversible lithium capacity and substantial charge/discharge rates. [233]. Boron nitride (BN) nanostructures are classified as a distinct category of nanomaterials due to their minimal toxic effects, excellent mechanical properties, excellent heat conductivity, and remarkable chemical and structural resilience [234-235].

Following the discovery of fullerenes, fullerene-like boron nitride nanomaterials have garnered significant interest [236]. $\text{B}_{12}\text{N}_{12}$ synthesized by Oku et al., recognized as the smallest nanocage consisting of tetragonal BN rings interspersed with hexagonal BN rings, has received considerable attention [237]. Due to its significant bandgap energy of 4 to 6 eV, boron nitride (BN) is typically classified as an insulator and is rarely utilized in energy storage and conversion. In addition, the π -electrons demonstrate limited mobility due to the weak delocalization of the atomic orbitals, resulting in a lack of sufficient electronic density [238-239]. The band gap can be, however, modulated through a selective functionalization, including chemical or physical alterations, hence enhancing the electronic conductivity and cation- π interactions crucial for alkali-ion storage capacities [240-243]. In this study, we systematically employed DFT calculations to evaluate the

concurrent improvement of electrical characteristics and anodic voltage performance of boron nitride nanocages via functionalization with various conducting polymers (CPs). The investigation focused on the contribution of polyacetylene (PA), poly-p-phenylene (PPPh), polythiophene (PT), and polypyrrole (PP) polymers known for their significant conductivity and electro-structural properties in improving the $B_{12}N_{12}$ anodic performance of Li^+ and Na^+ ion-based batteries.

5.2 computational details

A comprehensive electronic and structural analysis was performed on the boron nitride nanocage ($B_{12}N_{12}$), a selection of conducting polymers (CPs) comprising three repeating units, and the functionalized cluster of CP- $B_{12}N_{12}$ (Fig. 1), both with and without the inclusion of Li/Li^+ and Na/Na^+ . This was carried out using the DMol3 module within the Material Studio software suite [148]. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) was used to calculate the electron exchange-correlation energy, as it is known to be a reliable functional for accurately predicting electronic properties and adsorption energies [149-152]. The Double Numerical Plus Polarization (DNP+) basis set was employed, with each basis function restricted to a global orbital cut-off radius of 4.5 Å. To account for van der Waals interactions, the Grimme dispersion correction (DFT-D3) was applied, and a smearing value of 0.005 Ha was used to determine orbital occupancy [153-155]. For structural optimization, parameters such as the global orbital cut-off, displacement, maximum force, and self-consistent field (SCF) were set to 5.2 Å, 0.002 Å, 0.001 Ha/Å, and 1.0×10^{-6} Ha, respectively, to ensure high accuracy and energy convergence.

The adsorption energies of mono-valent atoms/ions on B₁₂N₁₂ and functionalized conducting polymers (CP-B₁₂N₁₂) were calculated using the equation presented below [140]:

$$E_{ad} = E_{complex} - [E_{B_{12}N_{12}/CPS-B_{12}N_{12}} + E_{(M/M^{n+})}] \quad (1)$$

where E_{ad} , $E_{complex}$, $E_{B_{12}N_{12}/CPS-B_{12}N_{12}}$, and $E_{(M/M^{n+})}$ represents, respectively, the total adsorption energy, adsorption energy of metal atom/ion on the nanocage (B₁₂N₁₂) or CP-B₁₂N₁₂, the total energy of pristine B₁₂N₁₂ nanocage or CP-B₁₂N₁₂, and the energy of the isolated metal atoms/ions. The change in energy gap ($\%E_g$), to evaluate the effective interaction and adsorption sensitivity resulting from the adsorption of different metal atoms/ions on B₁₂N₁₂ and/or CP-B₁₂N₁₂ was calculated as:

$$\%E_g = \left[\frac{E_{g_{complex}} - E_{g_{B_{12}N_{12}}}}{E_{g_{B_{12}N_{12}}}} \right] \times 100\% \quad (2)$$

where E_g , $E_{g_{complex}}$ and $E_{g_{B_{12}N_{12}}}$ represent the energy gaps of B₁₂N₁₂ or CP-B₁₂N₁₂, the complex, and that of the B₁₂N₁₂ after adsorbing E_{M/M^+} , respectively. In addition, the initial cell voltage (V_{cell}), was computed in similar fashion to our previous work [140] using the Nernst equation given as:

$$V_{cell} = \frac{-\Delta G_{cell}}{zF} \quad (3)$$

In this context, V_{cell} , ΔG_{cell} , z , and F denote the initial cell voltage, Gibbs free energy, the charge of the electrolytic cations (M⁺), and Faraday's constant (96500 C/mol or 23.061 kcal/volt·mol), respectively. Furthermore, ΔG_{cell} term can be evaluated by considering the effect of entropy contribution and volume negligible (<0.01V) [149] according to the equation below:

$$\Delta G_{cell} = \Delta E_{cell} + P\Delta V - T\Delta S \quad (4)$$

Hence, $\Delta G_{cell} \approx \Delta E_{cell}$, where ΔE_{cell} is the variation in the adsorption energies of the $B_{12}N_{12}$ and/or CP- $B_{12}N_{12}$ being examined. The formation energy (E_{form}) for the $B_{12}N_{12}$ nanocage and the CP- $B_{12}N_{12}$ were calculated as follows [156]:

$$E_{form} = \left[\frac{E_{B_{12}N_{12}} - E_{12B} - E_{12N}}{24} \right] \quad (5)$$

$$E_{form} = \left[\frac{E_{CP-B_{12}N_{12}} - E_{nx}}{T_{nx}} \right] \quad (6)$$

where $E_{B_{12}N_{12}}$ and $E_{CP-B_{12}N_{12}}$ represent the total energies of the bare nanocage and the conducting polymer-functionalized nanocage, while E_N , E_B , E_{nx} , and T_{nx} denote the total energies per atom of isolated nitrogen atoms, solid boron, isolated sulfur, hydrogen, and carbon atoms in the polymer, as well as the total number of atoms in the complex, respectively. The sign and magnitude of the formation energies indicate the level of stability of the system. The work function (Φ) is another key parameter that can give insights into the minimum energy required to remove one electron from the Fermi level [157-158]. The work function can be estimated using the theoretical methods proposed by Wu et al. [157] as follows:

$$\Phi = V_{el(+\infty)} - EF \quad (7)$$

$$EF = \left[\frac{E_{HOMO} - (E_{HOMO} - E_{LUMO})}{2} \right] \quad (8)$$

where E_{HOMO} and E_{LUMO} , EF , and $V_{el(+\infty)}$ denote the energies of the highest occupied and lowest unoccupied molecular orbitals, the Fermi level energy, and the energy of the electron outside the surface of the metal/ion- $B_{12}N_{12}$ or CP- $B_{12}N_{12}$ systems. Since $V_{el(+\infty)} \approx 0$. Therefore, Φ can be estimated as:

$$\Phi = -EF \quad (9)$$

5.3 Results and Discussion

5.3.1 Structural impact of functionalization on B₁₂N₁₂ nanocage features

The optimal configuration of B₁₂N₁₂ nanocage comprises six tetragonal and eight hexagonal BN rings (**Fig. 5.1**) that conform to the isolated tetragonal rule [244]. The B-N bond lengths calculated in hexagonal rings adjacent to four-membered rings ($BN_{6-4} = 1.49$ Å) and hexagonal rings adjacent to other six-membered rings ($BN_{6-6} = 1.45$ Å) are in agreement with previously reported [245-246]. For a comparison purpose, two heterocyclic, one homocyclic aromatic, and one acyclic nonaromatic CPs were selected, aiming to evaluate the influence of various configurations and the presence of heteroatoms on the electrical characteristics of functionalized nanocages and their corresponding anodic voltage (**Fig. 5.2**). Furthermore, the formation energy of the nanocage and the conducting polymer-functionalized nanocages were estimated. The negative formation energy value of -7.9 eV/atom confirms the sufficient stability of the nanocage. Furthermore, the negligible changes in the formation energies after the functionalization with various CPs (**Fig. 5.3**) indicate the favorable formation of these complexes.

The optimized structures of CP functionalized B₁₂N₁₂ are shown in **Fig. 5.2**. Before functionalization, the stability of attachments via the B and N atoms was estimated. The calculated formation energies were estimated to be -7.182 and -7.056 eV for functionalization via B and N atoms respectively, suggesting that the more stable functionalization is via the boron atom. As discussed earlier, the computed average B-N bond lengths in the tetragonal and hexagonal rings of B₁₂N₁₂ are 1.49 and 1.45 Å respectively. While no significant changes were observed in B-N bond of the nanocage after functionalization with most of the conducting polymers, a slight increase in B-N bond distance was observed in the hexagonal ring of the nanocage upon functionalization with

the heterocyclic PP. This can be attributed to the influence of lone pairs of electrons on nitrogen atoms. Such heteroatoms act in resonance with the cage, resulting in extending electron delocalization features and hence a slight increase in the bond length [247]. Furthermore, the B-N bond distance in the tetragonal and hexagonal rings of the cage remains almost unchanged in the case of $\text{Li@B}_{12}\text{N}_{12}$ and $\text{Na@B}_{12}\text{N}_{12}$ complexes. However, for the ionic counterparts, a slight decrease can be noticed in the B-N distance of the tetragonal ring of the cage particularly for the $\text{Li}^+\text{@B}_{12}\text{N}_{12}$ complex, while no changes were observed for $\text{Na}^+\text{@B}_{12}\text{N}_{12}$. The shortening in bond length can be attributed to the stronger interaction between Li-ion and the nanocage [248]. For $\text{M@CP-B}_{12}\text{N}_{12}$ complexes, no significant changes were observed in the B-N bond lengths in the tetragonal and hexagonal rings of the cage (**Table 5.1**). However, a shorter B-N bond length, particularly in the hexagonal ring was observed in the case of $\text{Li}^+\text{@PA-B}_{12}\text{N}_{12}$, $\text{Na}^+\text{@PPPh-B}_{12}\text{N}_{12}$, and $\text{Na}^+\text{@PT-B}_{12}\text{N}_{12}$ indicating a more prominent interaction as compared to the neutral metal counterpart. These various observations confirm the reasonable interactions of M/M^+ and the impact of polymers on the structural and electronic properties of the nanocage.

The calculated energy bands and HOMO-LUMO gaps of bare $\text{B}_{12}\text{N}_{12}$ nanocage and conducting polymer-functionalized nanocage ($\text{CP-B}_{12}\text{N}_{12}$) are compared in **Fig. 5.4**. Both energy and band gaps of bare $\text{B}_{12}\text{N}_{12}$ are 5.0 eV each, consistent with previously reported values [249]. However, these values notably decrease upon functionalization with various polymers. The simulated drop in energy gap ranges from highest to lowest in the order of 90% ($\text{PA-B}_{12}\text{N}_{12}$), 61% ($\text{PT-B}_{12}\text{N}_{12}$), 51% ($\text{PP-B}_{12}\text{N}_{12}$), and 42% ($\text{PPPh-B}_{12}\text{N}_{12}$), indicating a significant enhancement in the electronics properties of the $\text{B}_{12}\text{N}_{12}$ via

interfacing with various types of CPs. The predicted HOMO-LUMO energy gaps range between 2.90 to 0.46 eV, aligned with previously documented findings [250-251]. The significant reduction in the band gap indicates a change between the conduction and valence bands, thereby improving electron mobility [252]. The prominent reduction in the energy gap due to the non-aromatic PA functionalization indicates the greater perturbation of its π -electron system and the pronounced conjugation effect as compared to other aromatic counterparts. Similarly, poly-*p*-phenylenes exhibited the least effect on the band gaps, likely due to the lack of heteroatoms with lone pairs as compared to PT and PP polymers.

Furthermore, certain global reactivity characteristics, including chemical potential (μ), electronegativity (χ), hardness, softness (η), and electrophilicity (ω), can be utilized to evaluate the effects of functionalization on the nanocage (**Table 1** and **Fig. 5.5**). The chemical reactivities were estimated utilizing Parr and Pearson theories [166]. The chemical potential indicates the propensity of electrons to escape from a system, whereas chemical hardness reflects the resistance to changes in charge density distribution and is closely associated with the reactivity and stability of the molecular system [167]. The hard/soft acid/base (HSAB) theory suggests that molecules with greater hardness are less reactive due to a lower propensity for electron transfer during interactions. In contrast, soft substances with low η values facilitate more efficient electron transport. The global electrophilicity index (ω), established by Parr et al. [166], is calculated using chemical potential and hardness. It can be seen that PA-B₁₂N₁₂ exhibits the highest softness, chemical potential and electronegativity, electrophilicity as well as the lowest hardness value as compared to other CPs- B₁₂N₁₂ counterparts. This might be attributed to the

backbone type of PA and hence the extended linear conjugation nature, allowing for efficient electron delocalization. On the contrary, the $B_{12}N_{12}$ and PP- $B_{12}N_{12}$ nanocages exhibited the least values of chemical potential, electronegativity, electrophilicity but a high hardness value. Such a rating assesses the energy diminution achieved through optimal electron transport between the donor and acceptor. To have more insight into such a phenomenon, the total density of state TDOS and band structures of $B_{12}N_{12}$ and CP- $B_{12}N_{12}$ were explored (**Fig. S3**). The TDOS and band structure indicates that the newly generated energy levels are proximate to the Fermi energy level due to the functionalization with CP chains, confirming the reasonable interaction between the CP and $B_{12}N_{12}$. Furthermore, the decrease in conduction and valence band of the CP- $B_{12}N_{12}$ upon functionalization would improve charge transfer properties and thus the overall electronic reactivities of the complexes, likely to result in an enhanced potential cell voltage.

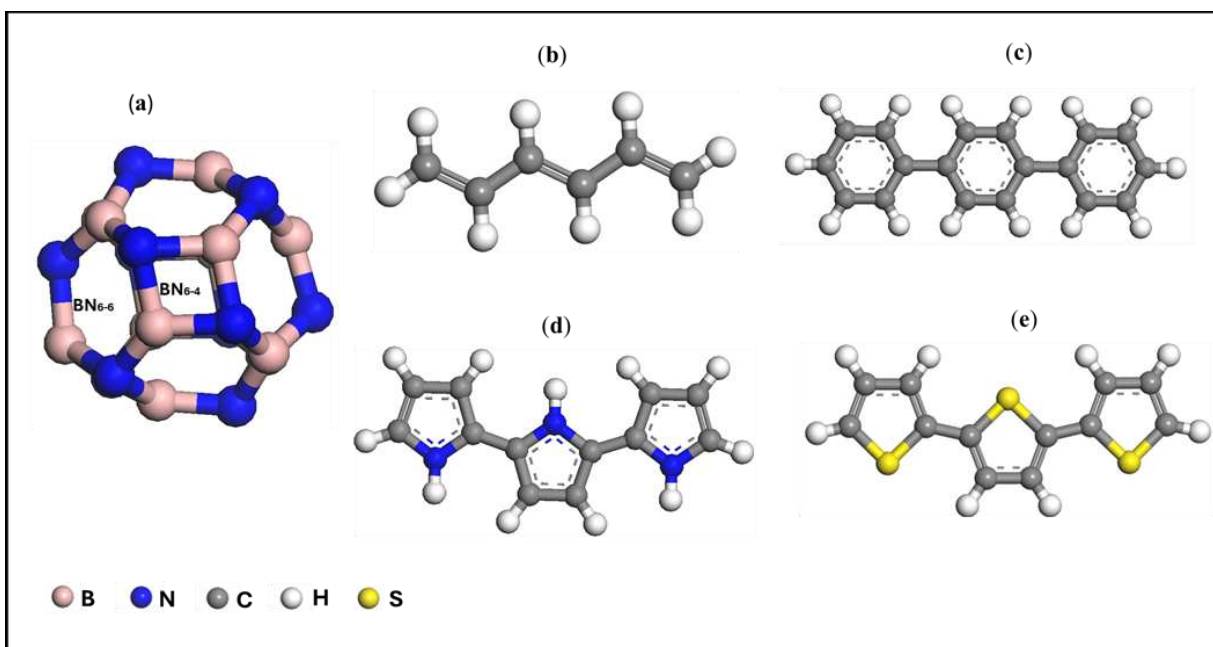


Figure 5.1 Geometrically optimized structures of (a) pristine $B_{12}N_{12}$ nanocage, (b) polyacetylene (PA), (c) poly-p-phenylene (PPPh), (d) polypyrrole (PP), and (e) polythiophene (PT) polymers.

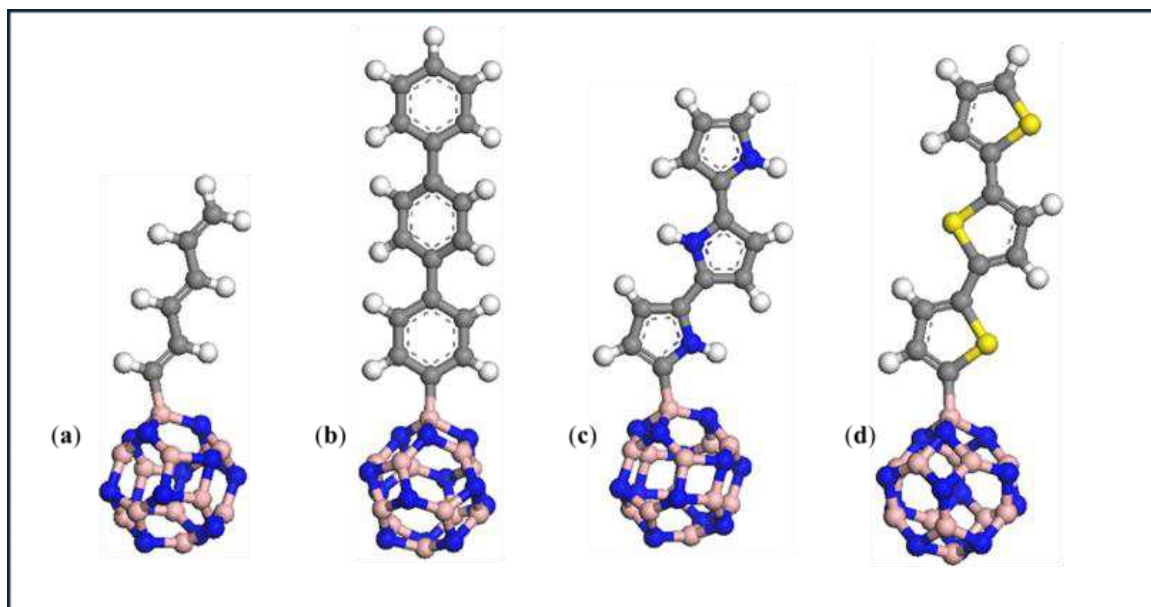


Figure 5.2 The optimized structures of conducting polymer functionalized $B_{12}N_{12}$ nanocages, namely, (a) PA- $B_{12}N_{12}$, (b) PPPh- $B_{12}N_{12}$, (c) PP- $B_{12}N_{12}$, (d) PT- $B_{12}N_{12}$.

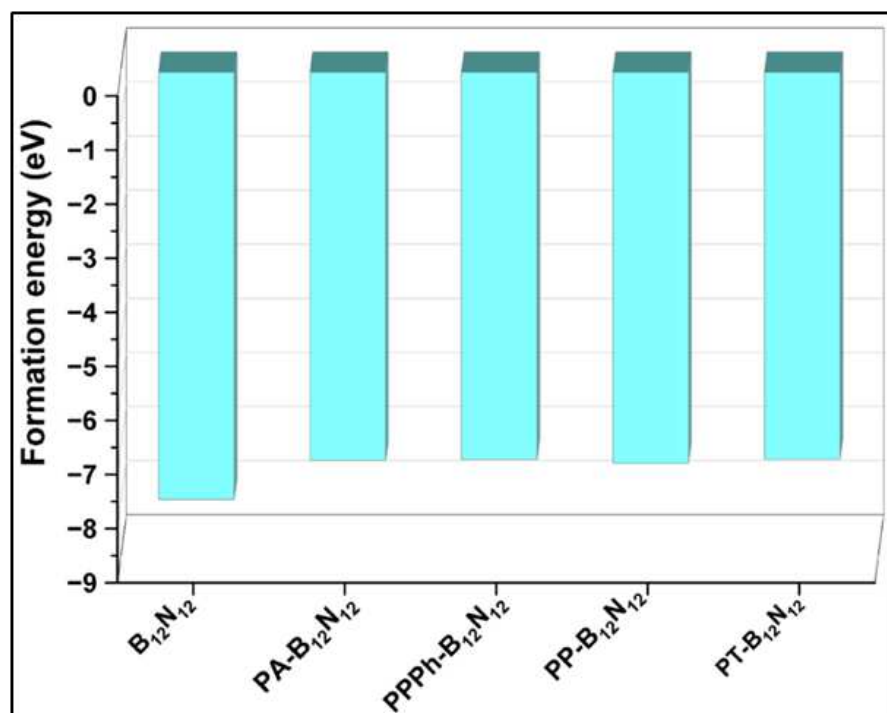


Figure 5.3 Estimated formation energies of bare $B_{12}N_{12}$ and functionalized PA- $B_{12}N_{12}$, PPPh- $B_{12}N_{12}$, PP- $B_{12}N_{12}$, and PT- $B_{12}N_{12}$ complexes showing insignificant changes after functionalizing which depicts the stability of the complexes.

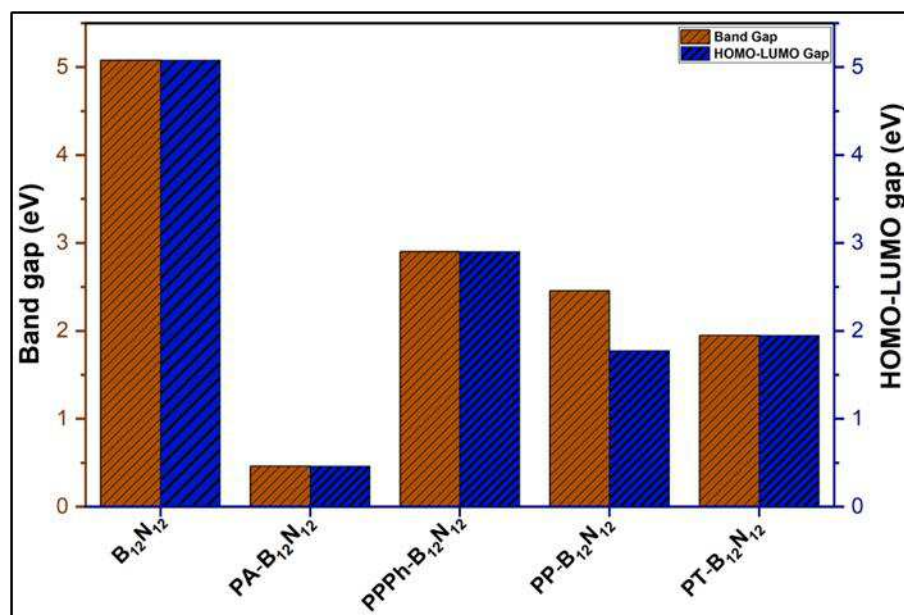


Figure 5.4 Calculated energy band and HOMO-LUMO gaps of pristine $B_{12}N_{12}$ as compared with CP-functionalized nanocages.

Table 5.1 Calculated boron to nitrogen bond distance in tetragonal and hexagonal rings, ionization potential (IP), electron affinity (EA), energy gap (Eg), Hardness (η), and electronegativity (χ) of the bare boron nitride nanocage, CPs functionalized boron nitride nanocage, CPs functionalized boron nitride nanocages, $M/M^+@B_{12}N_{12}$ and $M/M^+@CP-B_{12}N_{12}$, all in electron volt (eV).

Complex	B-N Bond distance (Å)		IP	EA	E _g	η	χ
	BN ₆₋₆	BN ₆₋₄					
B ₁₂ N ₁₂	1.45	1.49	7.112	2.036	5.077	2.538	4.575
PA-B ₁₂ N ₁₂	1.46	1.48	6.040	5.577	0.464	0.232	5.809
PPPh-B ₁₂ N ₁₂	1.45	1.49	5.903	3.002	2.901	1.450	4.453
PP-B ₁₂ N ₁₂	1.51	1.48	5.101	2.645	2.456	1.228	3.873
PT-B ₁₂ N ₁₂	1.50	1.49	5.515	3.568	1.947	0.973	4.542
Li@B ₁₂ N ₁₂	1.44	1.49	3.904	2.366	1.538	0.769	3.135
Li ⁺ @B ₁₂ N ₁₂	1.45	1.42	8.549	3.930	4.619	2.309	6.239
Li@PA-B ₁₂ N ₁₂	1.45	1.48	5.877	2.987	2.890	1.445	4.432
Li ⁺ @PA-B ₁₂ N ₁₂	1.40	1.49	7.684	4.937	2.746	1.373	6.310
Li@PPPh-B ₁₂ N ₁₂	1.44	1.49	5.772	2.535	3.237	1.619	4.153
Li ⁺ @PPPh-B ₁₂ N ₁₂	1.41	1.49	7.052	4.146	2.906	1.453	5.599
Li@PP-B ₁₂ N ₁₂	1.44	1.49	4.733	1.988	2.745	1.372	3.361
Li ⁺ @PP-B ₁₂ N ₁₂	1.42	1.48	6.366	3.794	2.571	1.286	5.080
Li@PT-B ₁₂ N ₁₂	1.44	1.49	5.313	3.163	2.149	1.075	4.238
Li ⁺ @PT-B ₁₂ N ₁₂	1.42	1.48	6.678	4.638	2.040	1.020	5.658
Na@B ₁₂ N ₁₂	1.45	1.49	6.585	3.107	3.479	1.739	4.846
Na ⁺ @B ₁₂ N ₁₂	1.44	1.49	8.454	4.365	4.088	2.044	6.410
Na@PA-B ₁₂ N ₁₂	1.44	1.47	5.744	2.832	2.912	1.456	4.288
Na ⁺ @PA-B ₁₂ N ₁₂	1.41	1.49	7.516	4.753	2.763	1.382	6.135
Na@PPPh-B ₁₂ N ₁₂	1.45	1.48	5.730	2.511	3.220	1.610	4.120
Na ⁺ @PPPh-B ₁₂ N ₁₂	1.40	1.49	6.937	4.002	2.935	1.467	5.470
Na@PP-B ₁₂ N ₁₂	1.45	1.48	4.746	2.040	2.706	1.353	3.393
Na ⁺ @PP-B ₁₂ N ₁₂	1.42	1.49	6.858	3.170	3.688	1.844	5.014
Na@PT-B ₁₂ N ₁₂	1.44	1.49	5.294	3.122	2.172	1.086	4.208
Na ⁺ @PT-B ₁₂ N ₁₂	1.40	1.49	6.185	4.227	1.958	0.979	5.206

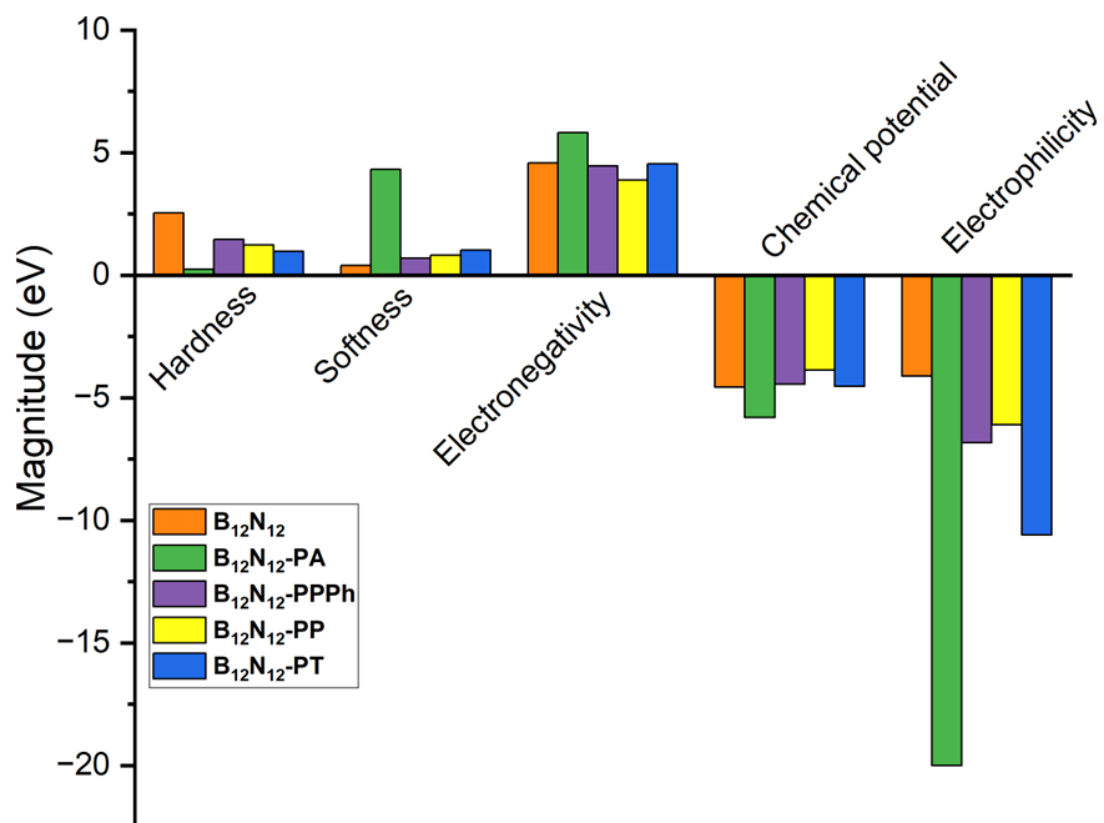


Figure 5.5 Comparison of the global reactivity descriptors of bare $B_{12}N_{12}$, with PA- $B_{12}N_{12}$, PPPh- $B_{12}N_{12}$, PP- $B_{12}N_{12}$, and PT- $B_{12}N_{12}$ complexes.

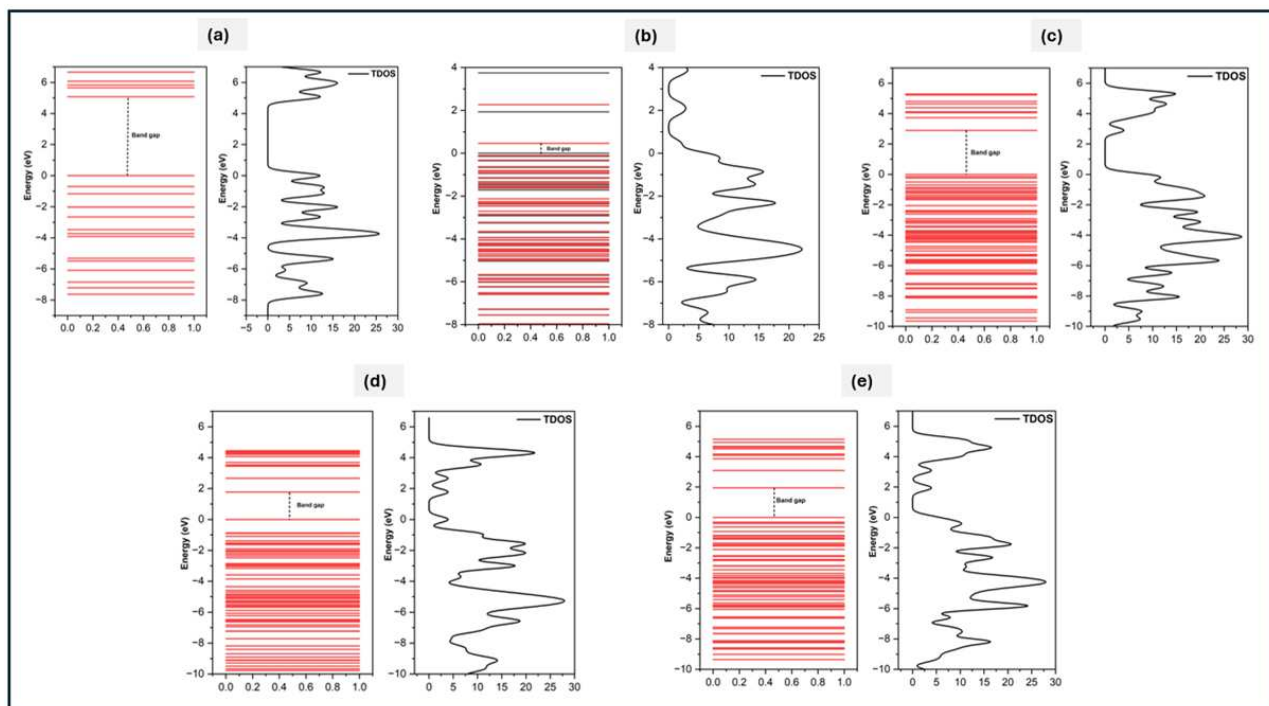


Figure 5.6 The band structure and total density of state of (a) bare $B_{12}N_{12}$ nanocage (b) PA- $B_{12}N_{12}$, (c) PPPh- $B_{12}N_{12}$, (d) PP- $B_{12}N_{12}$, and (e) PT- $B_{12}N_{12}$ showcasing the gap between the conduction and valence band before and after functionalization.

5.3.2 Adsorption characteristics of Li/Li⁺ and Na/Na⁺ on CP-B₁₂N₁₂

The adsorption properties of Li/Li⁺ and Na/Na⁺ on the B₁₂N₁₂ and CP-B₁₂N₁₂ surfaces were investigated by positioning the metals with their monovalent ions at various sites of the nanocages to compare the energetics of various configurations. Additionally, these metals or ions were placed at some selected positions at the CP-nanocage interface. Namely, two positions were tested: close to the CP (position A) and away from the CP (position B), as shown in **Fig. 5.7**. It was noticed that in the case of the bare nanocage, both metal and metal ions prefer to position close to the nitrogen atom (**Fig. 5.8**), while upon functionalization, particularly with PA and PPPh, the structures relax with the metal and metal ions being in the vicinity of the six-membered ring of the nanocage. Interestingly, the functionalization with heteroatom-containing PP and PT polymers exhibited a contrary behavior as the atoms/ions preferred to relax again above the nanocage nitrogen (**Fig. 5.7**). Generally, it is predicted that metals/ions adsorption in close proximity to the CPs exhibited a more stable state, indicating the significant impact of functionalization. This can be explained in terms of charge transfer facilitation throughout the polymer chains, strengthening the electrostatic interaction between the metal ion and the nanocage, thereby increasing the adsorption feasibility [253]. Due to the lone pair of electrons, sulfur and nitrogen atoms in PT and PP can bring about some polarized environment, thus the ions adsorbed tend to migrate in the neighborhood of the CP, facilitating stronger ion-polymer interactions. The adsorption energies of Li⁺ and Na⁺ ions on pristine B₁₂N₁₂ displayed higher negative values than that of the corresponding metal atoms (**Table 5.2**); however, the adsorption energies of neutral metal atoms on CP-B₁₂N₁₂ are more negative than that of their cation counterparts, which aligned with the reports in literature [140]. The observed counter behavior through incorporating CPs is noteworthy, indicating their impact on the metal ion

mobility. The enhanced stability of the Li/Na interaction in $M/M^+@CP-B_{12}N_{12}$ can be associated to the charge delocalization in CP, exhibiting strong interactions between their electrons and the unpaired s electron of the metals. These behaviors highlight the reflection of the influence of polymer functionalization on the nanocage, typically enhancing the charge transfer and conductivity.

In addition, the diffusion pattern of Li^+ and Na^+ ions were depicted in **Figs. 5.9 and 5.10** which illustrate the diffusion coefficients and the plot of mean square deviation against time steps, respectively. In the case of Li ions, PP and PT polymers functionalized nanocage exhibit larger diffusion coefficient values (10.8 and $11.9\text{ cm}^2/S^2$) than the corresponding PA, PPPh, and bare nanocage (7.1 , 10.4 and $8.6\text{ cm}^2/S^2$, respectively). The presence of heteroatoms in PT and PP can thus contribute to a wide-ranging electronic behavior and enhanced charge mobility through the electrostatic interaction with BN nanocages, leading to a more favorable environment for the diffusion via the polymer chains. Similarly, the flexibility of PT and PP in terms of their backbone conformations allows a more pronounced ionic diffusion over the surface [254]. In addition to the high diffusion values of PP, PT, and PPPh functionalized nanocages, their diffusion curves exhibit linear patterns, while the $PA-B_{12}N_{12}$ and bare nanocages demonstrate a contrary behavior. On the other hand, sodium ions encounter a lower diffusion than lithium, which can be understood in terms of their larger ionic radius, allowing lithium ions to migrate more effectively through the material. Furthermore, the higher charge density of lithium ions allows for a stronger interaction with the electron cloud either for the polymers or the boron nitride nanocage. Yet, this interaction can create a faster exchange mechanism with the polymer matrix, enhancing its diffusion rate [255]. This generally leads to nonlinearity

characteristics observed in various diffusion patterns of Na^+ in bare nanocages as well as in CP functionalized ones.

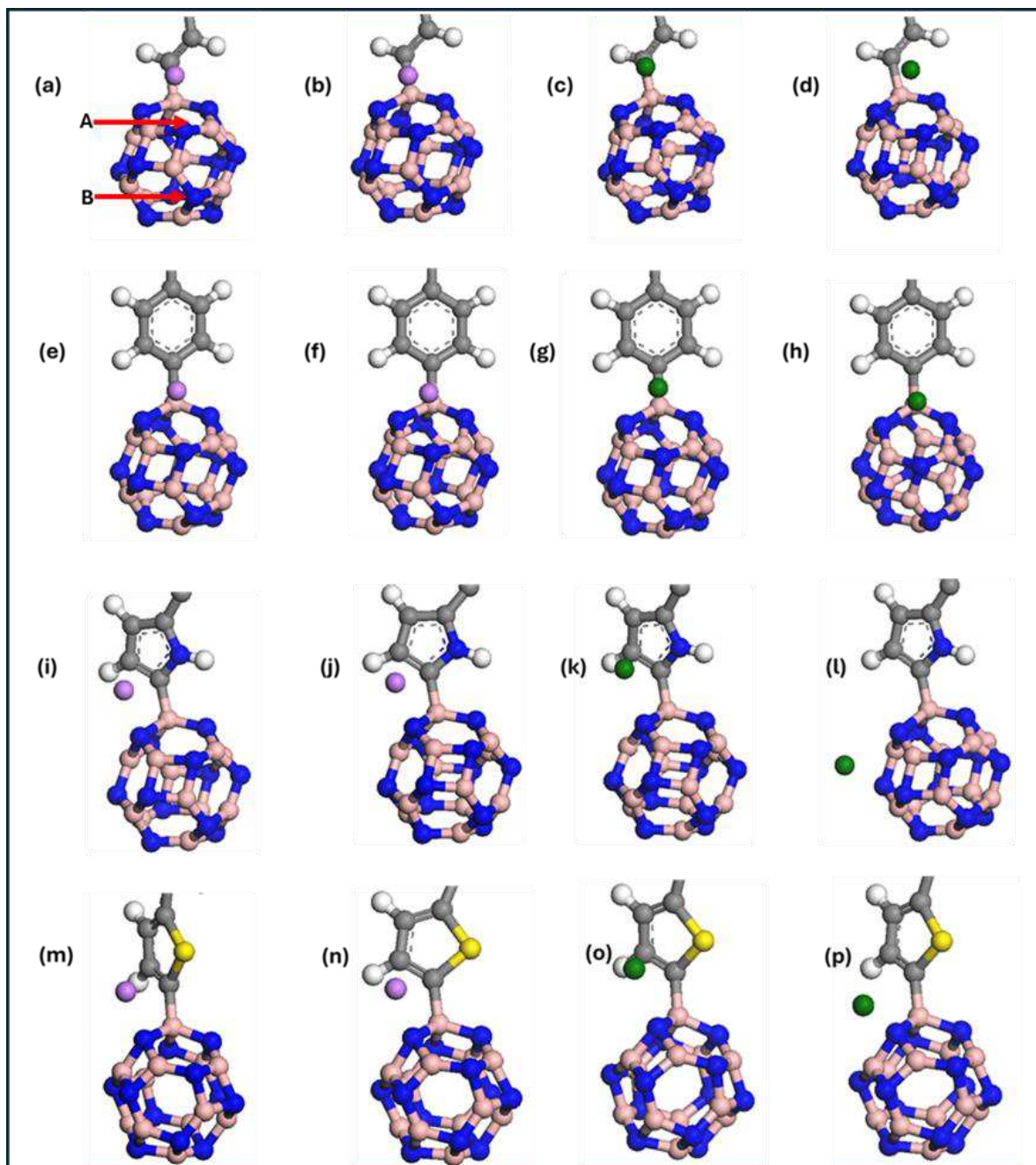


Figure 5.7 Optimized adsorption structures of monovalent metals/ions on CP functionalized nanocages, namely (a) $\text{Li@PA-B}_{12}\text{N}_{12}$ (b) $\text{Li}^+\text{@PA-B}_{12}\text{N}_{12}$, (c) $\text{Na@PA-B}_{12}\text{N}_{12}$, (d) $\text{Na}^+\text{@PA-B}_{12}\text{N}_{12}$, (e) $\text{Li@PPPh-B}_{12}\text{N}_{12}$, (f) $\text{Li}^+\text{@PPPh-B}_{12}\text{N}_{12}$, (g) $\text{Na@PPPh-B}_{12}\text{N}_{12}$, (h) $\text{Na}^+\text{@PPPh-B}_{12}\text{N}_{12}$, (i) $\text{Li@PP-B}_{12}\text{N}_{12}$, (j) $\text{Li}^+\text{@PP-B}_{12}\text{N}_{12}$, (k) $\text{Na@PP-B}_{12}\text{N}_{12}$, (l) $\text{Na}^+\text{@PP-B}_{12}\text{N}_{12}$, (m) $\text{Li@PT-B}_{12}\text{N}_{12}$, (n) $\text{Li}^+\text{@PT-B}_{12}\text{N}_{12}$ (o) $\text{Na@PT-B}_{12}\text{N}_{12}$, (p) $\text{Na}^+\text{@PT-B}_{12}\text{N}_{12}$.

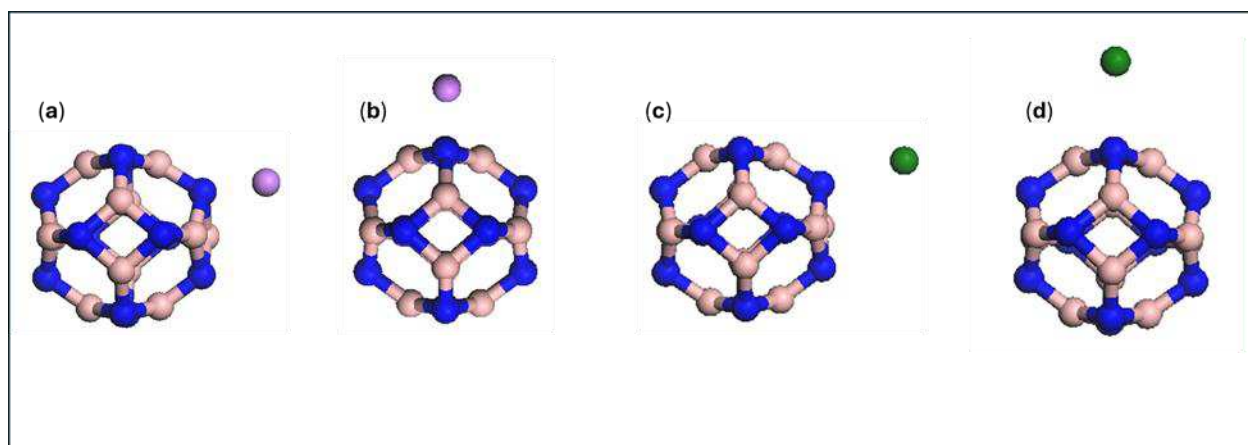


Figure 5.8 The optimized adsorption structures of monovalent metals/ions on CPs functionalized nanocage, namely, (a) $\text{Li@B}_{12}\text{N}_{12}$ (b) $\text{Li}^+\text{@B}_{12}\text{N}_{12}$, (c) $\text{Na@B}_{12}\text{N}_{12}$, (d) $\text{Na}^+\text{@B}_{12}\text{N}_{12}$.

Table 5.2 Calculated adsorption energies and binding distances of metals and metal ions on B₁₂N₁₂ and CPs functionalized B₁₂N₁₂ at different positions closed and away from the functionalized conducting polymer.

Complex	Position A		Position B	
	Adsorp. Energy (Kcal/mol)	Binding distance (Å)	Adsorp. Energy (Kcal/mol)	Binding distance (Å)
Li@B ₁₂ N ₁₂ (above N atom)	-34.411	1.921	-	-
Li@B ₁₂ N ₁₂ (above B atom)	-31.780	2.118	-	-
Li@B ₁₂ N ₁₂ (above ring)	-25.529	1.791	-	-
Li@B ₁₂ N ₁₂ (inside ring)	0.190	-	-	-
Li ⁺ @B ₁₂ N ₁₂ (above N)	-57.031	1.933		
Na@B ₁₂ N ₁₂ (above N atom)	-15.515	2.596	-	-
Na@B ₁₂ N ₁₂ (above B atom)	-12.866	3.003	-	-
Na@B ₁₂ N ₁₂ (above ring)	-10.422	2.012	-	-
Na@B ₁₂ N ₁₂ (inside ring)	9.077	-	-	-
Na ⁺ @B ₁₂ N ₁₂ (above N)	-43.346	2.602	-	-
Li@PA-B ₁₂ N ₁₂ (above N atom)	-109.963	1.884	-82.929	1.860
Li@PA-B ₁₂ N ₁₂ (above B atom)	-97.553	2.343	-91.344	2.396
Li@PA-B ₁₂ N ₁₂ (above ring)	-110.336	1.814	-91.344	1.592
Li@PA-B ₁₂ N ₁₂ (inside ring)	-74.773	-	-	-
Li ⁺ @PA-B ₁₂ N ₁₂ (above ring)	-14.728	1.700	-	-
Na@PA-B ₁₂ N ₁₂ (above N atom)	-86.976	2.468	-75.204	2.560
Na@PA-B ₁₂ N ₁₂ (above ring)	-94.138	2.364	-81.559	2.312
Na ⁺ @PA-B ₁₂ N ₁₂ (above ring)	-2.353	2.197	-	-
Li@PPPh-B ₁₂ N ₁₂ (above N atom)	-98.847	2.119	-98.644	2.283
Li@PPPh-B ₁₂ N ₁₂ (above ring)	-109.386	1.598	-92.175	1.78
Li ⁺ @PPPh-B ₁₂ N ₁₂ (above ring)	-23.024	1.874	-	-
Na@PPPh-B ₁₂ N ₁₂ (above N atom)	-90.780	2.254	-90.797	2.651
Na@PPPh-B ₁₂ N ₁₂ (above ring)	-97.021	2.266	-84.853	2.258
Na ⁺ @PPPh-B ₁₂ N ₁₂ (above ring)	-12.732	2.385	-	-
Li@PP-B ₁₂ N ₁₂ (above N atom)	-96.737	1.911	-76.968	2.243

Li@PP-B ₁₂ N ₁₂ (above ring)	-88.985	1.702	-69.092	1.944
Li ⁺ @PP-B ₁₂ N ₁₂ (above N atom)	-30.378	1.887	-	
Na@PP-B ₁₂ N ₁₂ (above N atom)	-79.120	2.337	-64.661	2.545
Na@PP-B ₁₂ N ₁₂ (above ring)	-70.896	2.317	-61.246	2.26
Na ⁺ @PP-B ₁₂ N ₁₂ (above N atom)	-15.265	2.531	-	-
Li@PT-B ₁₂ N ₁₂ (above N atom)	-104.719	1.923	-104.235	1.954
Li@PT-B ₁₂ N ₁₂ (above ring)	-102.929	1.836	-83.447	1.618
Li ⁺ @PT-B ₁₂ N ₁₂ (above N atom)	-27.625	1.900	-	-
Na@PT-B ₁₂ N ₁₂ (above N atom)	-87.236	2.330	-91.900	2.331
Na@PT-B ₁₂ N ₁₂ (above ring)	-85.210	2.446	-75.406	2.263
Na ⁺ @PT-B ₁₂ N ₁₂ (above N atom)	-6.490	2.579	-	-

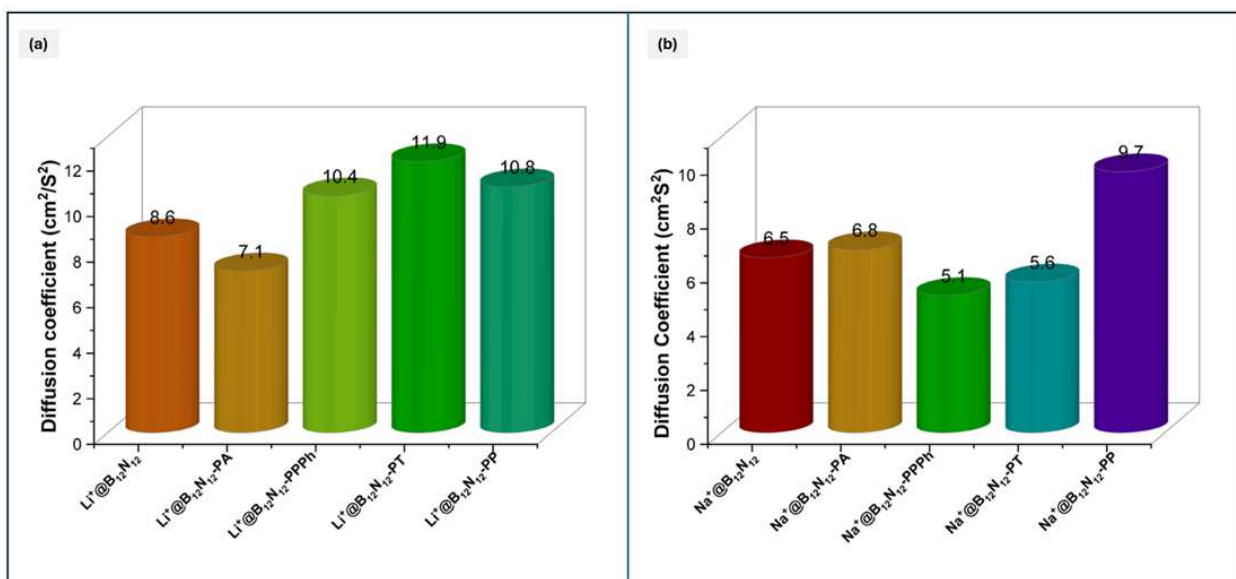
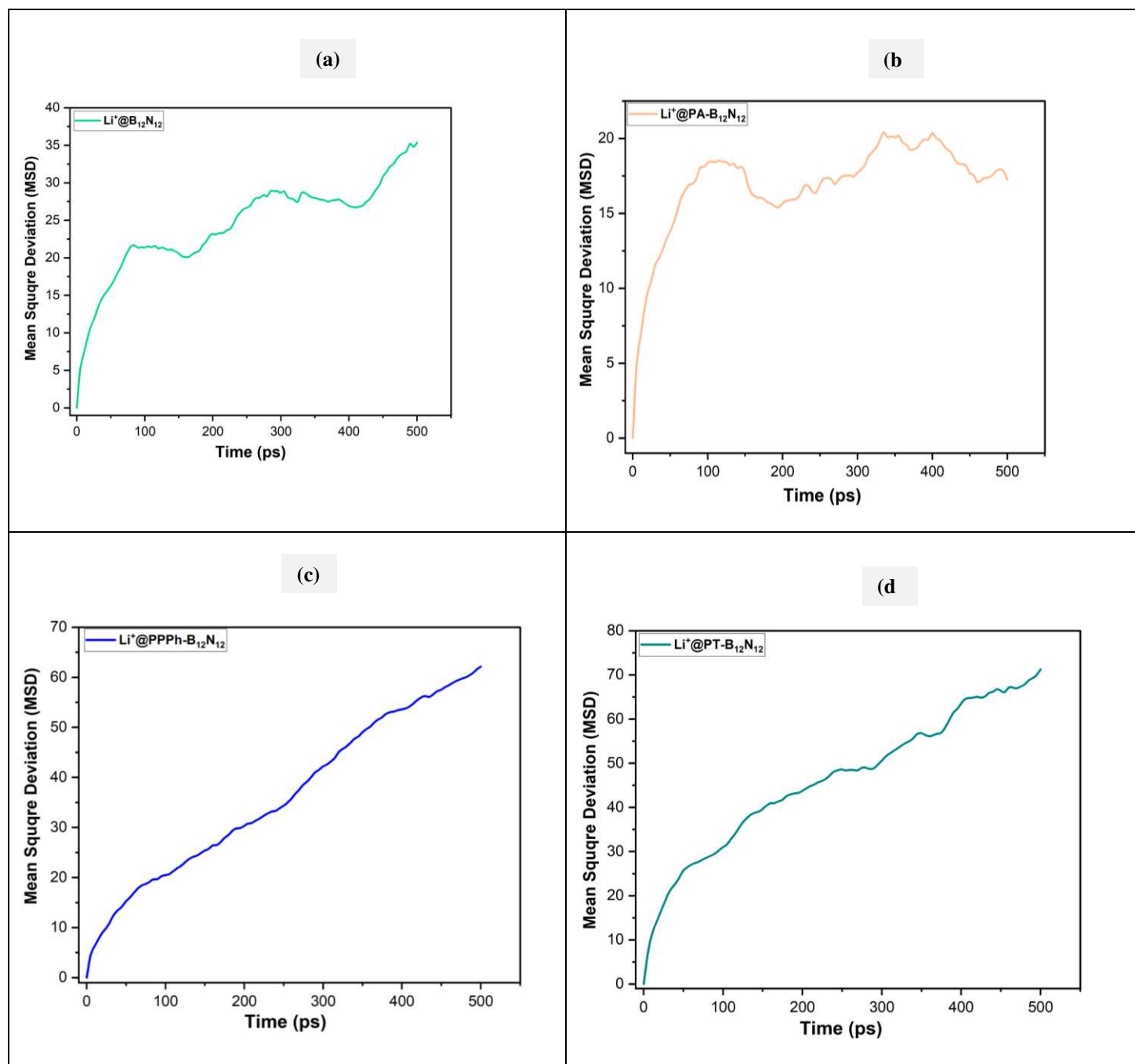
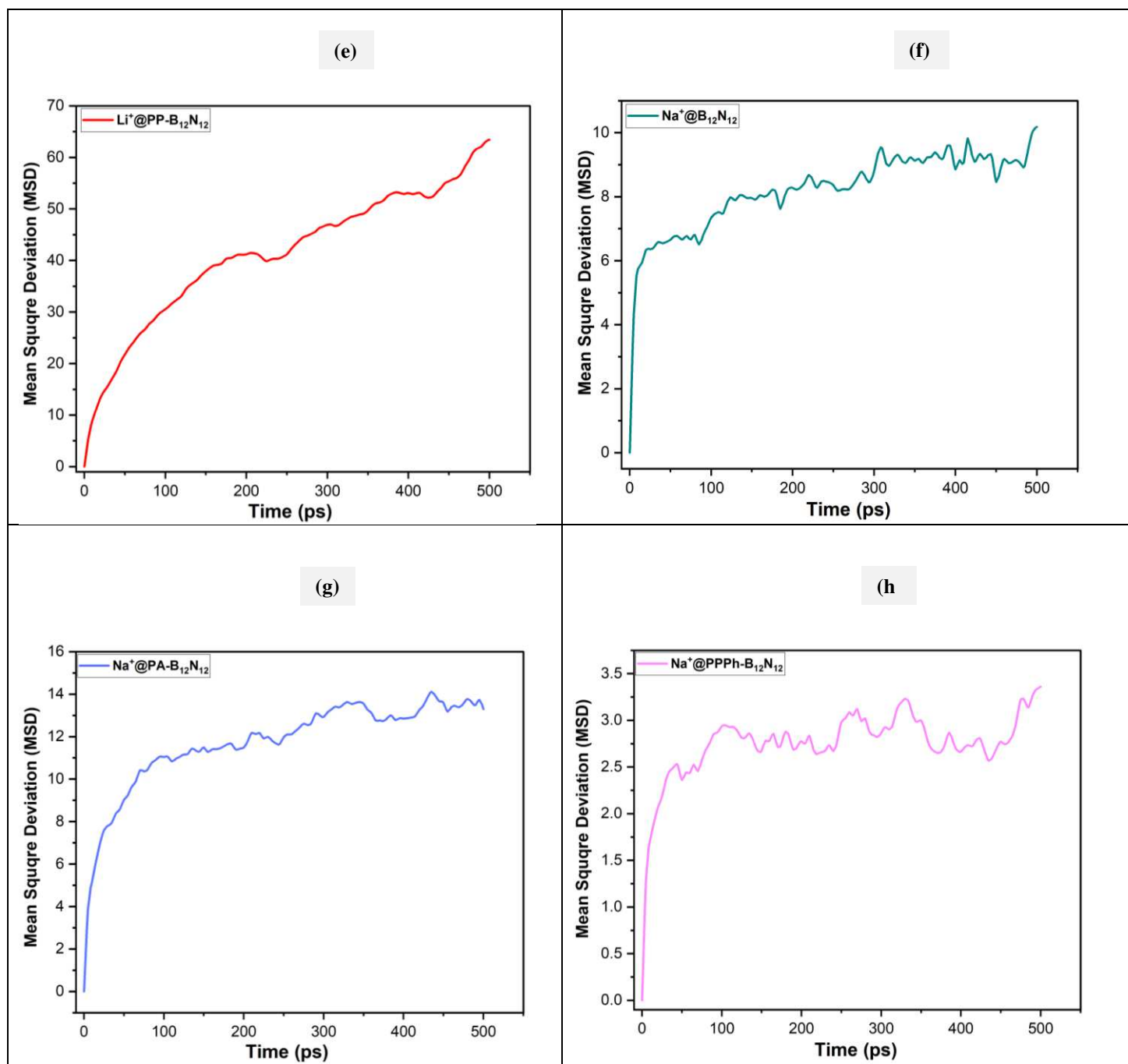


Figure 5.9 Diffusion coefficients values of (a) Li⁺@B₁₂N₁₂ and Li⁺@CP-B₁₂N₁₂, and (b) Na⁺@B₁₂N₁₂ and Na⁺@CP-B₁₂N₁₂





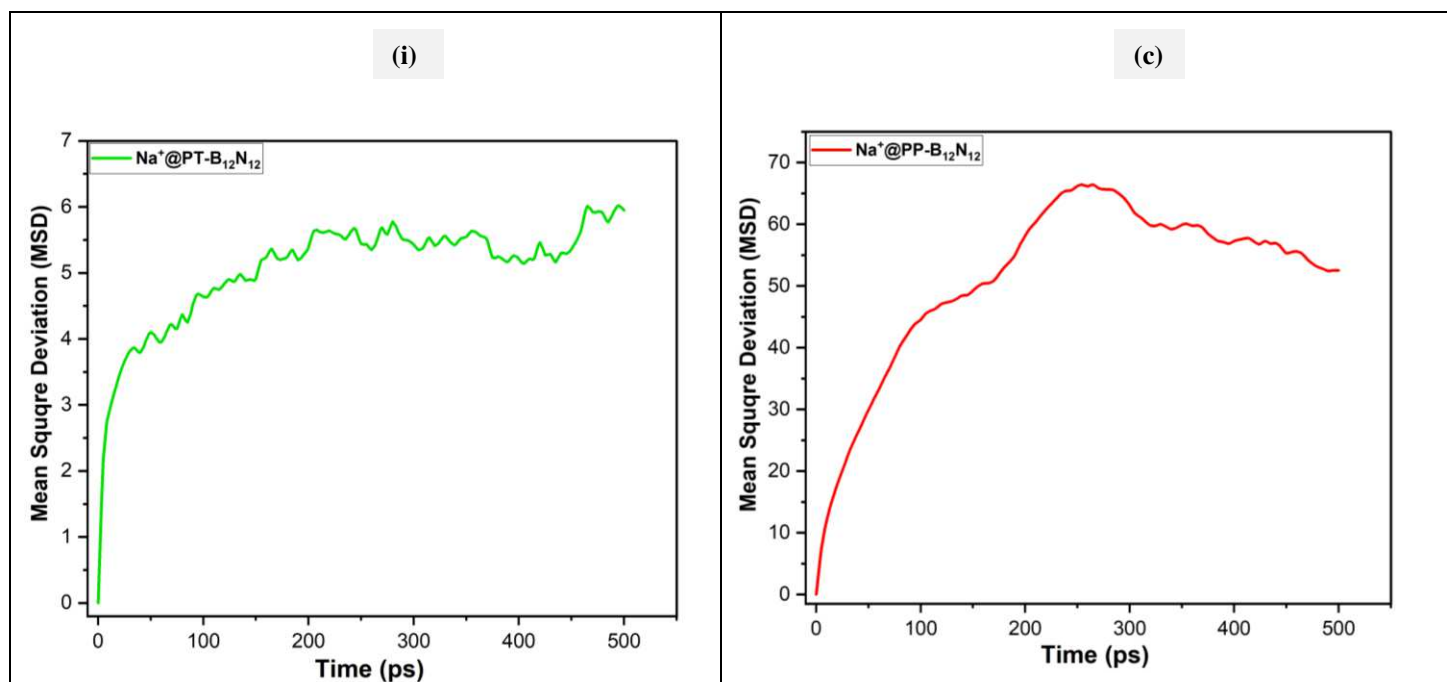


Figure 5.10 Depicts diffusion pattern of various metal ions across various complexes namely, (a) $\text{Li}^+@B_{12}N_{12}$, (b) $\text{Li}^+@PA-B_{12}N_{12}$, (c) $\text{Li}^+@PPPh-B_{12}N_{12}$, (d) $\text{Li}^+@PT-B_{12}N_{12}$ (e) $\text{Li}^+@PP-B_{12}N_{12}$, (f) $\text{Na}^+@B_{12}N_{12}$, (g) $\text{Na}^+@PA-B_{12}N_{12}$, (h) $\text{Na}^+@PPPh-B_{12}N_{12}$, (i) $\text{Na}^+@PT-B_{12}N_{12}$, (j) $\text{Na}^+@PP-B_{12}N_{12}$

5.3.3 Anodic performance of B₁₂N₁₂ and CP-B₁₂N₁₂ nanocages

The working principle of Li⁺/Na⁺ based batteries in the presence of CP-B₁₂N₁₂ nanocages as anodic material base can be depicted graphically in **Fig. 5.11**. Considering B₁₂N₁₂ as an anode in the metal ion batteries, the associated half-cell and overall cell reactions occurring at the anode and cathode can be presented as follows:

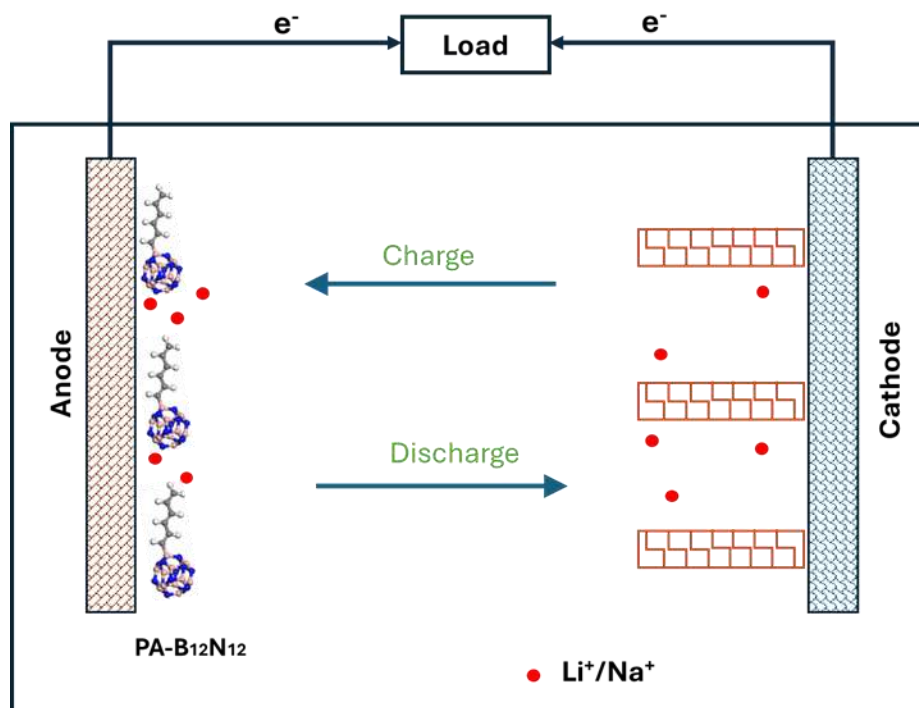
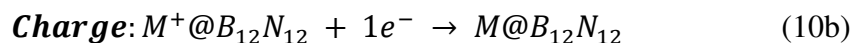
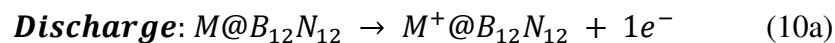
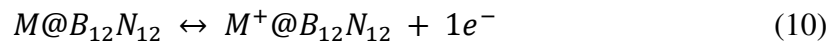


Figure 5.11 Schematic representation showing the working principle of Li-ion (LIBs) and Na ion (NIBs) batteries in the presence of CP-B₁₂N₁₂ nanocage structure as an anodic material.

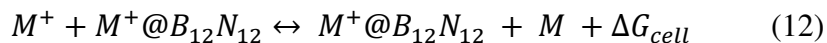
At anode:



At cathode:



Overall cell reaction:



Furthermore, the computed ΔE_{cell} and the corresponding cell voltage values resulting from the adsorption of M/M^+ on $B_{12}N_{12}$ and CP- $B_{12}N_{12}$ structures are compared in **Fig. 5.12**. While a bare nanocage exhibited a less pronounced adsorption energy, a significant increase following the functionalization with different polymers can be noticed. This signifies the role of CPs in the interaction between metal or metal ions and the nanocage itself, which is then translated into cell voltage. A noticeable reduction in adsorption energy results upon going from M^+ ions to neutral atoms due to the intrinsic charge on the metal ions. Nonetheless, lithium encounters a slightly stronger adsorption to the nanocage than sodium as a result of its smaller atomic/ionic size. The V_{cell} of $Li@B_{12}N_{12}$ complex was estimated to be 0.98 V, in agreement with previously reported values [256]. For PA functionalized $B_{12}N_{12}$, the designed LIBs and SIBs exhibited the most improved values of 4.14 V and 3.98 V, respectively, as compared to the other CPs (**Fig. 5.12**) and in line with other high-performing monovalent ion batteries reported in the literature [256,140]. Additionally, the PPPh, PP, and PT functionalized $B_{12}N_{12}$ nanocages all demonstrated an increase in cell voltages, recording values of 3.74, 2.87, and 3.34 V for LIBs, and 3.65, 2.76, and 3.50 V for SIBs, respectively. The decrease in cell voltage with the increasing size of metal ions consistently resulted from the functionalization with PA, PPPh, and PP. Polythiophene, however, seems not to interrupt the trend shown by the unfunctionalized $B_{12}N_{12}$, having the sodium ion performance outweigh that of lithium-ion

counterpart. The anomalous behavior observed in the case of PT- $B_{12}N_{12}$ can be attributed to the unique electronic properties of polythiophene, which exhibits sulfur-mediated charge transfer, leading to a more favorable interaction with the larger Na ion, thereby reversing the typical trend. In general, polyacetylene and poly-p-phenylene functionalized $B_{12}N_{12}$ exhibited the most promising cell voltage for both the designed LIBs and NIBs. Generally, the energy gap between the conduction and valence bands is reduced through the functionalization of $B_{12}N_{12}$ nanocage with various polymers, which enhances the nanocage electrical properties and facilitates the electrochemical reversibility of metal ions at the electrodes. Consequently, it leads to improved charging and discharging rates, extended lifespan, and hence enhanced overall battery performance [257].

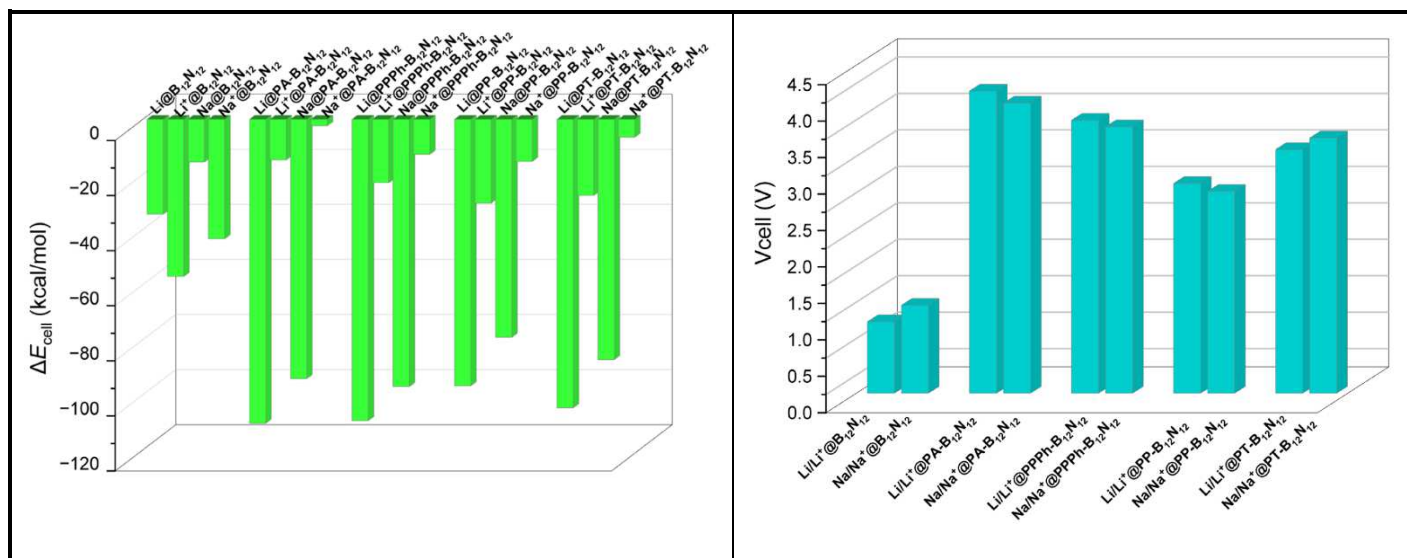
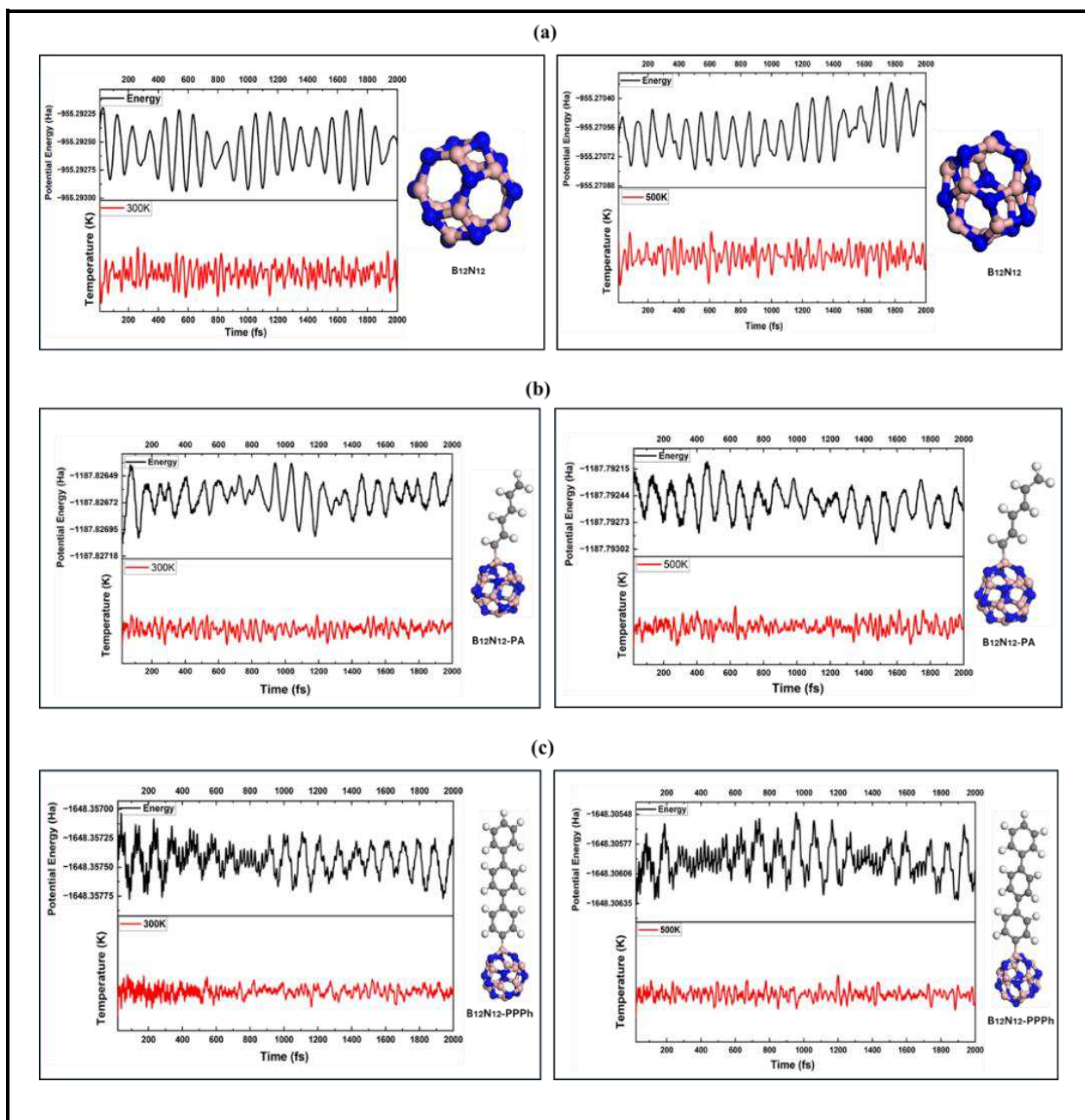


Figure 5.12. Computed adsorption energies, ΔE_{cell} (left) and cell voltages, V_{cell} (right) resulting from the adsorption of $M/M^+@B_{12}N_{12}$ and $M/M^+@CP-B_{12}N_{12}$.

5.3.4 Thermal stability

A major attribute impacting the feasibility of materials is their ability to preserve structural integrity within particular temperature ranges. Increased temperatures, frequently resulting from diverse reactions within batteries, can lead to deformations in electrode materials, thus diminishing the battery overall lifespan. Consequently, evaluating the temperature stability of electrode materials is crucial. Herein, we conducted molecular dynamic simulations to assess the thermal stability of $B_{12}N_{12}$ and CP- $B_{12}N_{12}$, as illustrated in **Fig. 5.13**. The time step of 0.5 fs for 2000 total steps, which corresponds to a simulation duration of 1 ps, was utilized. Testing $B_{12}N_{12}$ and various CP- $B_{12}N_{12}$ nanocages was conducted at 300 K and 500 K. For pristine $B_{12}N_{12}$ nanocage, a fluctuation in temperature was observed at 300 K, which was accompanied by a drift in potential energy at 500 K. Upon functionalization with various CPs, a notable decrease in temperature fluctuation was observed at 300 K and 500 K. Although a drift in potential energy was noticed for PT- $B_{12}N_{12}$ at 500 K, the structural integrity of various CP- $B_{12}N_{12}$ remained intact at both temperatures. Generally, the increase in thermal stability upon functionalization indicates the robust interfacial adhesion that promotes the stability of the material as compared to the non-functionalized nanocage. In addition, conducting polymer can improve thermal conductivity by providing a pathway for heat dissipation, thus reducing thermal stress on the nanocage and enhancing thermal stability.



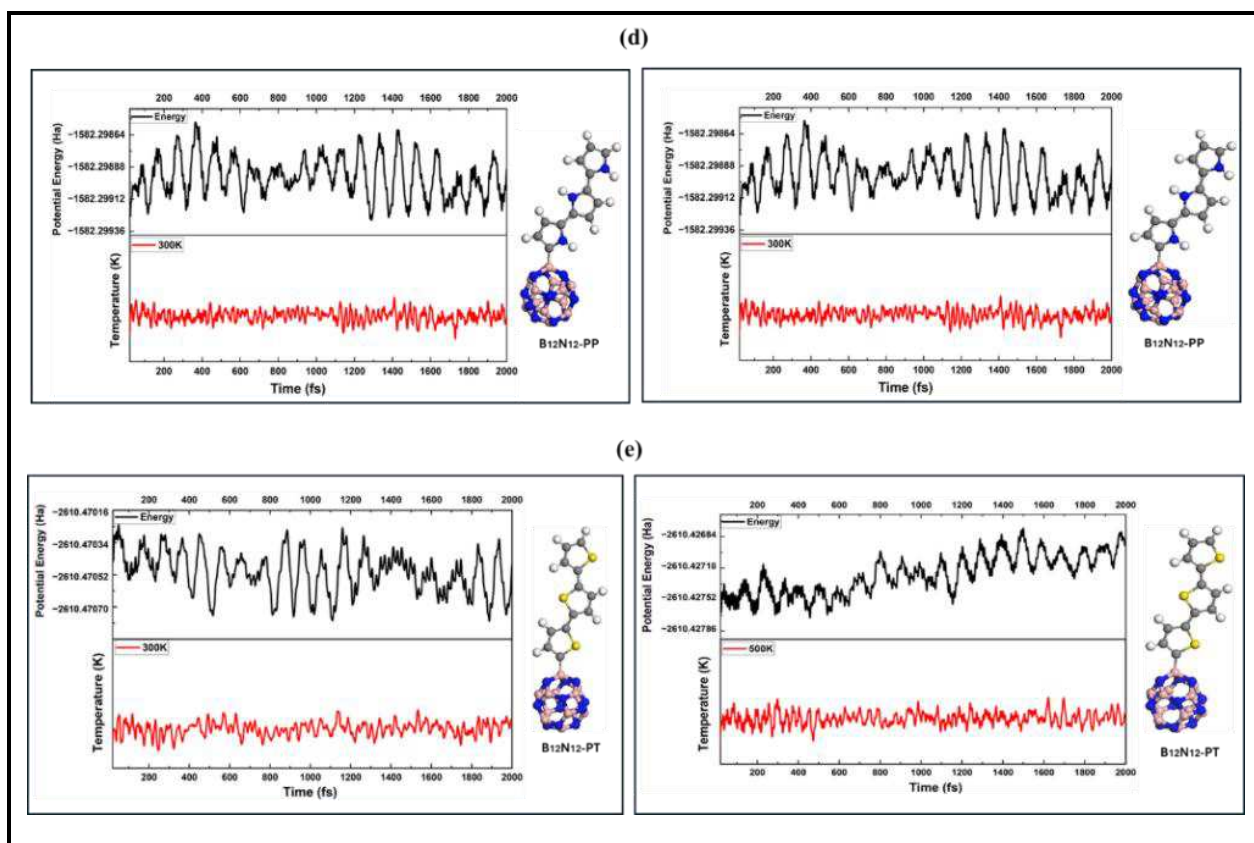


Figure 5.13 The simulated temperature dynamics and potential energy fluctuations with the corresponding final geometrical structures of (a) bare $B_{12}N_{12}$, (b) $PA-B_{12}N_{12}$, (c) $PPPh-B_{12}N_{12}$, (d) $PP-B_{12}N_{12}$, and (e) $PT-B_{12}N_{12}$ at 300 K and 500 K respectively.

CHAPTER 6

CONCLUSION.

This thesis has explored the first-principles density functional theory (DFT) calculations to investigate the functionalization of boron nitride nanosheets (BNNS), boron carbon nitride nanosheets (BCNNS) with the poly-p-phenylene (PPPh) conducting polymer and fullerene-like $B_{12}N_{12}$ nanocage with polyacetylene (PA), poly-p-phenylene (PPPh), polypyrrole (PP), and polythiophene (PT) conducting polymers. The effects of incorporating various electron-withdrawing and electron-donating groups such as hydroxyl, amino, cyano, methyl, methoxy, chloro, bromo fluoro, carboxyl, and nitro groups into PPPh-BNNS and PPPh-BCNNS were examined. These hybrid materials were further assessed as potential candidates for metal ion batteries.

The functionalization of various conducting polymers substantially enhanced the structural, electrical, and thermal properties of two-dimensional boron nitride nanosheets (2D BNNS), boron carbonitride nanosheets (BCNNS), and fullerene-like boron nitride ($B_{12}N_{12}$) nanomaterials. The nitro-functionalized PPPh-BNNS exhibited the most improved electronic properties, demonstrating a significant reduction of 63% in total energy and 58% in band gap upon functionalization. To further explore its applicability, we evaluated nitro-PPPh-BNNS as an anode material for lithium (Li), sodium (Na), beryllium (Be), and magnesium (Mg)-ion batteries. Global reactivity descriptors revealed significant improvements in the electronic properties of BNNS after functionalization. Notably, the cell voltage increased significantly for all studied systems: Li-ion (2.30 V to 3.66 V), Na-ion (1.62 V to 3.18 V), Be-ion (1.95 V to 3.14 V), and Mg-ion (4.73 V to 6.89

V). In addition, a theoretical specific capacity of 244 and 217 mAh/g and an average open-circuit voltage (OCV) of 2.73 V and 2.28 V were recorded for the designed LIBs and SIBs respectively. Similarly, the bromo-functionalized PPPh-BNNS demonstrated the most improved electronic properties in comparison with various electron-withdrawing and donating groups by increasing the nearly zero band gap of the BCNN by 14%. Thus, the applicability of the designed bromo-PPPh-BCNNS material was evaluated as an anode material for lithium (Li), sodium (Na), beryllium (Be), and magnesium (Mg)-ion batteries. The results show that the incorporation of the polymer enhances the ion diffusion which can improve efficiency, and overall lifespan by improving charge/discharge rates, increasing capacity, prolonging cycle life, ensuring safety, and optimizing the battery's efficiency. Global reactivity descriptors such as electronegativity (χ), and electrophilicity (ω), revealed significant improvements in the electronic properties of BCNNS after functionalization. Notably, the cell voltage increased significantly for all systems studied: Li-ion (1.05 V to 2.62 V), Na-ion (0.84 V to 2.59 V), Be-ion (5.94 V to 8.20 V), and Mg-ion (4.24 V to 6.02 V). In addition, a theoretical specific capacity of 248 and 223 mAh/g and an average open-circuit voltage (OCV) of 2.47 V and 1.96 V were recorded for the designed LIBs and SIBs respectively. The functionalization of the B₁₂N₁₂ nanocage with different conducting polymers (CPs), such as polyacetylene (PA), poly-p-phenylene (PPPh), polypyrrole (PP), and polythiophene (PT) resulted in an improvement in its electronic structure. The analysis demonstrated that the integration of CP substrates leads to significant reductions of around 90% for PA, 42% for PPPh, 51% for PP, and 61% for PT in the energy gaps. Their feasibility as prospective anodic materials in Li-ion and Na-ion batteries has been evaluated by quantum chemical descriptors and electronic properties.

The cell voltage demonstrated a notable elevation across all examined systems: PA-B₁₂N₁₂ (4.14 V and 3.98 V), PPPh-B₁₂N₁₂ (3.74 V and 3.65 V), PP-B₁₂N₁₂ (2.87 V and 2.76 V), and PT-B₁₂N₁₂ (3.34 V and 3.50 V) for the analyzed Li-ion and Na-ion batteries, respectively.

To conclude, the observed trend underscores the influence of the size and charge of metal ions in enhancing battery energy efficiency. These findings demonstrate the potential of nitro-functionalized PPPh-BNNS and bromo-functionalized PPPh-BCNNS as well as PA, PT, PPPh, and PP-functionalized B₁₂N₁₂ nanocage in improving the energy efficiency of Li, Na, Be, and Mg-ion batteries. This work provides valuable insights into the role of functionalized conducting polymers in the development of advanced, highly efficient energy storage materials. Further studies can explore the experimental synthesis and characterization of 2D BCN, BN nanosheets and the nanocage functionalized with conducting polymers, to validate the theoretical predictions obtained from DFT calculations. Additionally, investigating the electrochemical performance of these nanocomposites in metal-ion battery applications can provide valuable insights into their potential for practical implementation. Furthermore, exploring the scalability and feasibility of large-scale production of these nanocomposites can pave the way for their potential use in next-generation energy storage devices.

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Highlights

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VITAE

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Career Interest: Physical/Computational Chemistry and Spectroscopy.

EDUCATION

- **Bachelor of Science (Hons) Chemistry, Federal University Birnin Kebbi, Nigeria 2015-2019.**
- **Overall CGPA: 4.88/5.00 Percentage: 97% Remark: First Class Degree**
- **Master of Science in Physical/Computational Chemistry, King Fahd University of Petroleum and Minerals, 2022-2025**
- **Overall CGPA: 3.78/4.00**

AREA OF RESEARCH INTEREST

- Advanced materials for high-performance rechargeable batteries and solid-state energy storage systems.
- Mechanistic studies and catalyst development for efficient hydrogen evolution reaction (HER) in acidic and alkaline media.
- Computational modeling of materials and chemical processes (DFT, MD simulations)
- Surface science and catalysis for green and sustainable chemistry
- Quantum thermodynamics and noise-assisted quantum processes
- Light-matter interactions in biological and energy systems

COMPUTATIONAL CHEMISTRY SKILLS

- **Gaussian**
- **Material Studio**
- **VASP**
- **Quantum Espresso**

PUBLICATIONS

- Fathurrahman Nur Allif, **Shehu Mohammed**, Abdulaziz A. Al-Saadi *et al.* "The role of hydrogen bonding in the conformational stability of 2-methoxyresorcinol: Insights from theoretical calculations, SERS spectroscopy, and solvent effect." *Journal of Molecular Liquids* 414 (2024): 126201
- Esraa Kotob, **Shehu Mohammed** *et al.* Interplay of Morphology and Facet Orientation of Cu Nanocrystals Directing CO₂ Electroreduction To Value-added Products” *Energy Technology*- Under review
- **Shehu Mohammed** and Abdulaziz A. Al-Saadi. "Silver-modified titanium-based MXene as a promising SERS substrate for the characterization of cytotoxic agent cyclophosphamide: Experimental and DFT study." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 336 (2025): 126055
- Sajjad Hussain, **Shehu Mohammed**, Abdulaziz A. Al-Saadi *et al.* “Recent progress in first principles modelling of catalytic CO₂ reduction and water splitting reactions using transition metal-based 2D MOFs” *Materials Today Sustainability*
- **Shehu Mohammed**, Sajjad Hussain and Abdulaziz A. Al-Saadi. “Engineering anodic materials for metal-ion batteries with conducting polymer functionalized boron nitride nanocages: a DFT perspective” *ChemistrySelect*- Under review.

RESEARCH AND WORK EXPERIENCE

- Education officer at kwara state teaching service commission Ilorin Nigeria-**2021**.
- Volunteering: National Youth Service Corps Secondary school. 2018-2020.
- I learned and used basic spectroscopy techniques and chemical synthesis techniques for chemical research.
- Laboratory instructor and classroom teacher at MUWANSHAT COLLEGE OF HEALTH SCIENCES, Taraba State, Nigeria [NYSC] **2020 - 2021**.
- Taught over (250 students) in Chemistry; prepared laboratory procedures and experimental designs; conducted and graded tests and examinations; Organized extra curriculum lessons for over 50 students.
- Teaching Assistant at King Fahd University of Petroleum and Minerals: Teaches Principles of general Chemical Laboratory Sections – **2023**.
- Undergraduate Researcher, Federal University Birnin Kebbi, Nigeria. March 2019-August 2019
- Project Title: “. Evaluation of mechanical properties of polyethylene reinforced with coir fiber composite.”
- Description: The research aimed to produce a biodegradable composite material from polyethylene reinforced with coconut fiber and test the mechanical strength of the material, such as Young's modulus and tensile strength.
- Kaduna North water board, Chemical and water analysis Malali, Kaduna State [SIWES] (2018).

- Learned the basic and complex water treatment and purification, learned the laboratory analysis of water, test and treatment of water hardness and heavy metals.
- Gutagi Table water limited [SIWES] (2017).
- Learned pathological/physiological/biochemical investigations using complex procedures and producing table water for public usage.

LEADERSHIP AND VOLUNTEERING EXPERIENCE

- I was the Academic secretary of Student's Chemical Society of Nigeria Federal University Birnin Kebbi, Nigeria chapter. I volunteered and served in delivering tutorials for the undergraduate students in the Department of pure and Industrial Chemistry at Federal University Birnin Kebbi, Nigeria, with the intentions of strengthening the academic and moral aspect of the students and excellence certificate was awarded to me.
- I was also a member of the academic development committee of Muslims Students' Society of Nigeria (MSSN) FUBK Chapter (2019). I volunteered and served in delivering tutorials for the school of basic studies and undergraduate students at Federal University Birnin Kebbi, Nigeria with the intentions of strengthening the academic and moral aspects of the students.

DISTINCTIONS/HONOURS AND AWARDS

- Academic Secretary Student's Chemical Society of Nigeria, FUBK Chapter 2019
- Certificate of National Youth Service Corps (NYSC)
- Overall best graduating student of the Edu Local government students' association FUBK chapter (2019) with CGPA of 4.88) (2019)
- Member of academic development committee Muslims Students' Society of Nigeria (MSSN) FUBK Chapter (2019).
- Kwara State Government Scholarship (2015-2019)
- Overall best graduating student, Department of Pure and Industrial Student, Federal University Birnin Kebbi (2019).

RESEARCH GRANTS AND CONFERENCES ATTENDANCE.

- RETI 50K (Saudi Arabian Riyals) Grant Challenge Competition
- Chemistry poster presentation conference
- Global Student Research conference
- American Chemical Society 2025 Spring Conference (San Diego, CA, USA)

PROFESSIONAL AFFILIATIONS

- American Chemical Society
- Kwara State Teaching Service Commission.
- Member, Students' Chemical Society of Nigeria, Federal University Birnin Kebbi.

PERSONAL SKILLS

I.T. Skills: Microsoft Office™ tools; Word, Excel, and PowerPoint; SPSS.

English Proficiency: Efficient command of listening, reading, speaking, and writing skills

Other Skills: Research skills, Communication Skills, Project management, Leadership Skills

REFREES

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