Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Structural and Electronic properties of Li adsorbed single and bilayer porphyrin sheets as an electrode material for energy storage devices – A DFT Analysis

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The interlayer interaction energy between the bilayers are calculated using the formula,

$E_{interaction} = E_{bilayer} - (E_{layer1} + E_{layer2})$

Bilayer type	Interaction energy (eV)
AA1	-0.855
AA2	-0.794
AA3	-0.636

Table.S1 Interaction energy between the various bilayer structures.

Here, $E_{bilayer}$ denotes the total energy of the bilayer structure. E_{layer1} and E_{layer2} are the energy of layer 1 and layer 2 obtained from the optimized structure of bilayers.

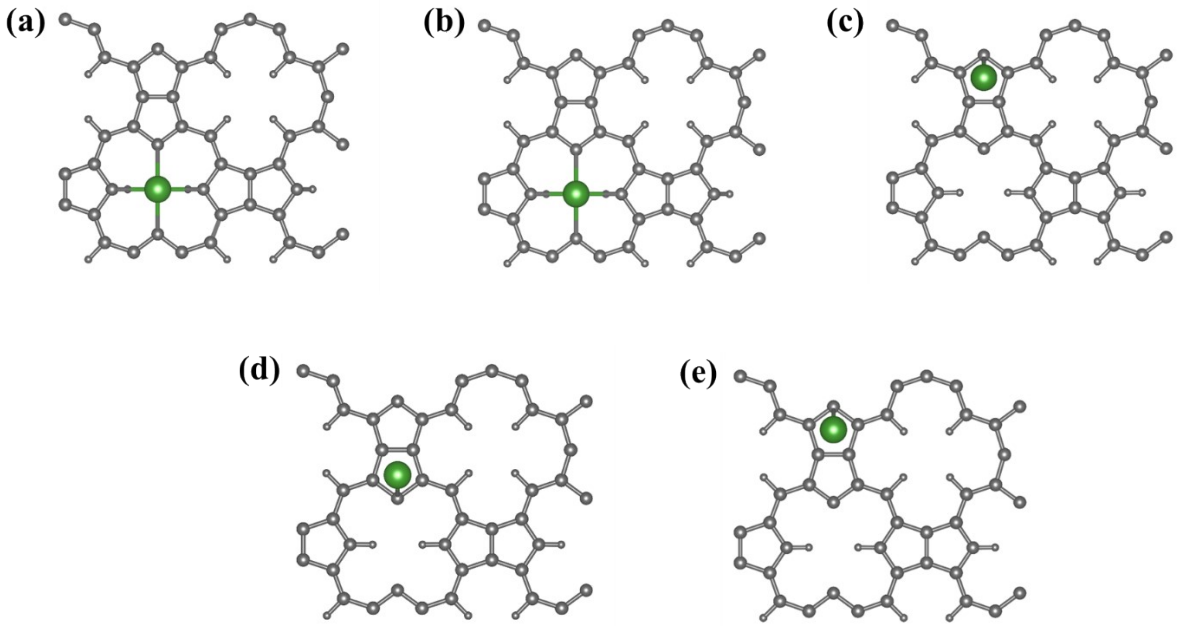

Fig.S1 Top view of the relaxed structures of Li atom adsorbed monolayer porphyrin sheet at site (a) S4, (b) S5, (c) S6, (d) S7, and (e) S8. The grey colour represents the Li atom.

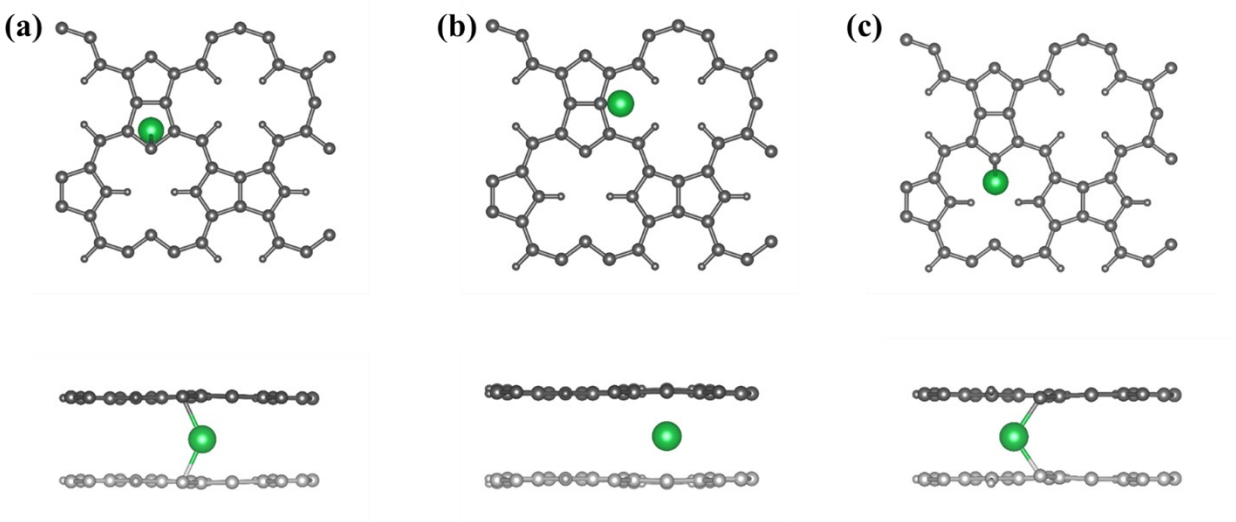

Fig.S2 Top and side view of the relaxed structures of Li atom intercalate within the bilayer porphyrin sheet AA3 at site (a) S1, (b) S2, and (c) S3, respectively. The green colour represents the Li atom.

System	Adsorption energy (kcal/mol)	Charge transfer |e|
S1	-75.95	0.842
S2	-64.87	0.866
S3	-89.17	0.875

Table.S2 Adsorption energy and charge transfer for various sites of Li intercalate within the bilayer of AA3 type.

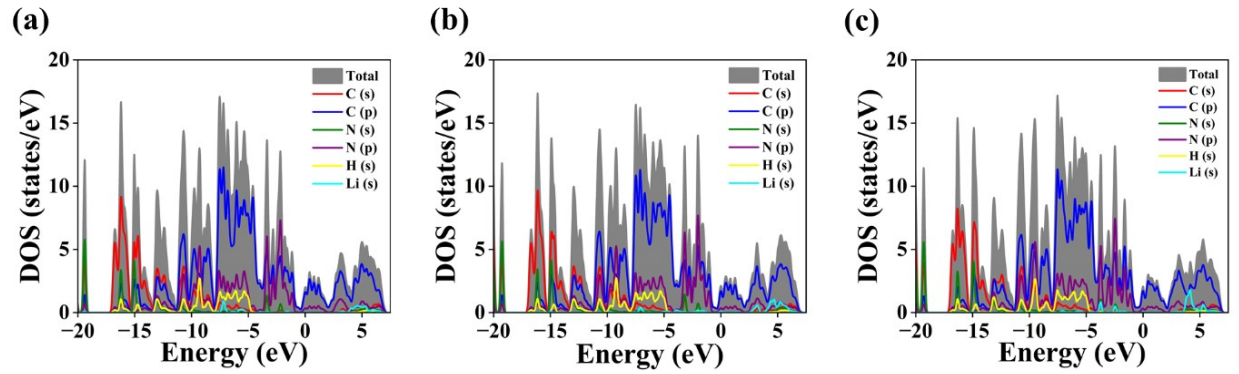

Fig.S3 The PDOS of Li atom adsorbs on BLP sheets AA3 at site (a) S1, (b) S2, and (c) S3, respectively.

Li^+ adsorption on PS

The Li^+ is subjected to interact with the PS at site S3, in order to get the adsorption interaction. The Li^+ is adsorbed at the height of 2.264 Å with the adsorption energy of 42.98 kcal/mol. The positive value indicate that the energy adsorbed in Li^+ at PS is endothermic while in the case of Li it is exothermic process. And the resultant value is very much lower than that of the adsorption energy of Li. The distinct initially charge levels of the lithium are responsible for the disparate adsorption energies between Li and Li^+. Less favorable adsorption energy results from higher electrostatic repulsion of the positively charged Li^+ from the PS surface. The charge transfer occurred 0.903 |e| after Li^+ was adsorbed on PS. Although the overall adsorption process

is less beneficial energetically, the larger charge transfer for Li^+ indicates a more substantial interaction, which could involve stronger chemical bonding. The convoluted interplay among the charge states of lithium and their interaction with the PS surface is highlighted by the combination of positive and negative adsorption energies and charge transfer values. The explanation for the observed trends in adsorption behavior should take into account both electronic and energetic aspects.

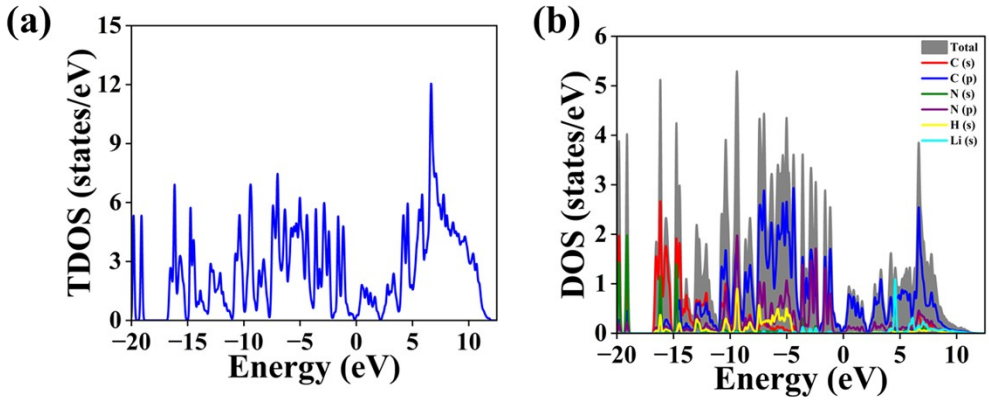

Fig.S4 The (a) DOS and (b) PDOS of Li^+ adsorbs on monolayer PS at site S3.

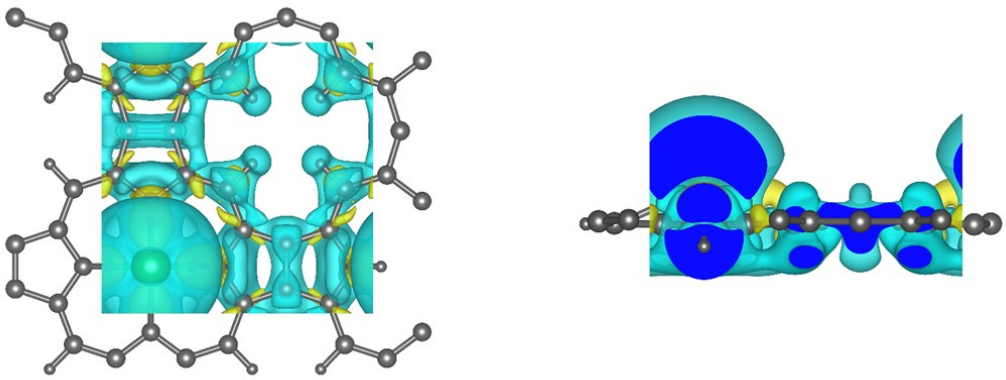

Fig.S5 The top and side view of charge density difference plots for Li^+ adsorbed on PS at site S3. The yellow and cyan colors represents charge accumulation and depletion

To get insight into the reactivity of the system, we consider charge transfer obtained during the adsorption process. The Fukui function of the charged system can be calculated using the formula,

$$f^{+}(Li^{+}) = \text{Charge transfer of } Li^{+} - \text{Charge transfer of Li}$$

Since, Li^{+} is adsorbed on the site S3, charge transfer of Li to the PS at site S3 has been chosen for this aspect. The calculated Fukui function is 0.051 |e|, the positive value suggest that the charged system is nucleophilic in nature.

Bilayer structures	Reaction potential (V)
AA1	-3.595
AA2	-3.736
AA3	-3.722

Li @ various sites of bilayer AA3	Reaction potential (V)
S1	-4.054
S2	-3.363
S3	-4.575

Table.S3 The calculated reaction potentials for Lithium adsorption over the various bilayer PSs.