

# Twisted Perylene Diimides with Tunable Redox Properties for Organic Sodium-Ion Batteries

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Organic rechargeable batteries gain huge scientific interest owing to the design flexibility and resource renewability of the active materials. However, the low reduction potentials still remain a challenge to compete with the inorganic cathodes. This study demonstrates a simple and efficient approach to tune the redox properties of perylene diimides (PDIs) as high voltage cathodes for organic-based sodium-ion batteries (SIBs). With appropriate electron-withdrawing groups as substituents on perylene diimides, this study shows a remarkable tunability in the discharge potential from 2.1 to 2.6 V versus Na<sup>+</sup>/Na with a sodium intake of  $\approx 1.6$  ions per molecule. Further, this study explores tuning the shape of the voltage profiles by systematically tuning the dihedral angle in the perylene ring and demonstrates a single plateau discharge profile for tetrabromo-substituted perylene diimide (dihedral angles  $\theta_1$  &  $\theta_2 = 38^\circ$ ). Detailed structural analysis and electrochemical studies on substituted PDIs unveil the correlation between molecular structure and voltage profile. The results are promising and offer new avenues to tailor the redox properties of organic electrodes, a step closer toward the realization of greener and sustainable electrochemical storage devices.

## 1. Introduction

Sodium ion batteries (SIBs) have been extensively studied in the recent past as an alternative to their lithium counterparts (LIBs), owing to concerns regarding cost and limited reserves of lithium. Particularly, in large-scale storage applications like hybrid vehicles and renewable power stations, SIBs, with the abundance and low cost of sodium, are more viable than LIBs.<sup>[1–6]</sup> Sodium exhibits electrochemical properties similar to that of lithium (0.3 V more positive) and its ionic radius is about 1.3 times to that of lithium ion. While the positive

potential offers better safety, it also lowers the reduction potential of the active materials.<sup>[7,8]</sup> Recently, several transition metal-based systems have been proposed as promising electrode materials for SIBs,<sup>[3,4]</sup> but high production costs and the associated environmental concerns question the long-term reliance on these materials. Also, the insertion of large Na<sup>+</sup> ions into rigid lattices results in multistep phase transitions and the materials often suffer from low capacity utilization or sluggish kinetics.<sup>[8,9]</sup>

Organic materials with promising features like light weight, design flexibility at the molecular level, good resource renewability and low production costs are emerging as promising alternatives to inorganic materials.<sup>[10–12]</sup> Recent reviews on organic materials show significant developments on radical and carbonyl based materials for batteries.<sup>[13,14]</sup> However, the low reduction potentials offered

by these materials compared to their inorganic counterparts outweigh all the merits.<sup>[15–17]</sup> With the inherent 0.3 V more positive reduction potential of Na than Li, it is even more challenging to achieve higher reduction potentials with organic materials for SIBs. Radical based materials offer the highest reduction potentials among organic materials for SIBs, but they depend on large anions like PF<sub>6</sub><sup>−</sup> and ClO<sub>4</sub><sup>−</sup> for charge compensation.<sup>[8,9]</sup> These large electrolyte anions cannot be readily inserted into active material and require large amounts of electrolyte while compromising the practical specific energy densities.<sup>[15,18]</sup> Carbonyl compounds, particularly carboxylate salts and anhydride-based materials, with their great diversity, can be tailored for desired properties.<sup>[19–23]</sup>

Redox potential of a molecule can be tailored by tuning its highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) energy levels. According to the molecular orbital theory, a lower LUMO level means higher electron affinity and thus a higher reduction potential for the molecule. Lowering the LUMO levels could be achieved in two ways. Attaching electron withdrawing groups to the redox active molecule is one way<sup>[15,24–27]</sup> and extending the conjugation in a molecule through aromatic rings is another conventional way.<sup>[10,21,28]</sup> Extending the conjugation could increase the electrochemical dead weight of the molecule and result in reduced theoretical capacity. Nevertheless, extended conjugation is expected to increase the ion intake and practical capacity of a

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