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Tarun Kumar Bharati
 Assistant Professor,
 Department of Chemistry,
 R.C.S. College, Manjhaul,
 Begusarai, Bihar, India

Electronic band alignment and charge storage capacity in organic semiconductor-MXene (Perylene-Ti₃C₂Tx) heterostructures through a theoretical study

Tarun Kumar Bharati

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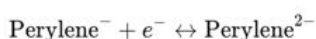
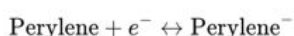
Abstract

Organic semiconductor-MXene heterostructures have emerged as versatile materials for energy storage and optoelectronic applications because of their tunable band alignment, high surface area, and superior charge transport properties. Among these, perylene-based organic semiconductors integrated with titanium carbide MXenes (Ti₃C₂Tx, where Tx represents surface groups -O, -OH, and -F) show particular promise, owing to their stable interfaces that promote efficient charge separation and storage. This work presents a theoretical study of the electronic band alignment and charge storage capacity of perylene-Ti₃C₂Tx heterostructures using density functional theory (DFT) and electronic structure analysis. The results reveal a type-II band alignment, with the perylene conduction band minimum aligned favorably with the MXene Fermi level, enabling efficient electron transfer. Surface functionalization strongly affects band bending, interface dipole formation, and electronic coupling. Oxygen-terminated Ti₃C₂Tx provides the most favorable conditions for charge transfer, whereas fluorine terminations suppress conductivity through electron localization. Projected density of states (PDOS) analysis confirms strong hybridization between perylene π orbitals and Ti-d states, enhancing interfacial communication. Charge density difference maps further show significant redistribution, indicating improved charge storage relative to pristine perylene or Ti₃C₂Tx. Capacitance values estimated from the density of states near the Fermi level suggest that perylene-Ti₃C₂Tx heterostructures could function as high-performance electrodes for supercapacitors and hybrid storage systems. Overall, the findings emphasize the importance of surface terminations and molecular orientation in designing optimized organic semiconductor-MXene heterostructures for future technologies.

Keywords: Organic semiconductors, MXene, perylene, Ti₃C₂Tx, band alignment, charge storage, heterostructures, DFT

Introduction

The rapid development of energy storage and optoelectronic technologies has created a strong demand for hybrid materials that can combine high charge transport, stable redox activity, and tunable molecular properties. Conventional inorganic semiconductors offer superior conductivity and electrochemical stability but often lack flexibility and molecular-level tunability. Organic semiconductors, in contrast, exhibit structural diversity, π -conjugated electron delocalization, and low-cost synthesis, but their limited intrinsic conductivity and charge storage capacity hinder large-scale applications. Therefore, hybrid systems that merge the complementary properties of organic and inorganic materials are of significant current interest. Among organic semiconductors, perylene derivatives represent an important class of electron-accepting aromatic systems. Their extended π -conjugation and high electron affinity allow them to participate in stable electron transfer and reversible reduction reactions. Perylene tetracarboxylic dianhydride (PTCDA) and related molecules have been widely studied in organic field-effect transistors (OFETs), dye-sensitized solar cells, and photodetectors. Importantly, perylene undergoes stepwise reduction reactions that can be exploited for charge storage:



Corresponding Author:
Tarun Kumar Bharati
 Assistant Professor,
 Department of Chemistry,
 R.C.S. College, Manjhaul,
 Begusarai, Bihar, India

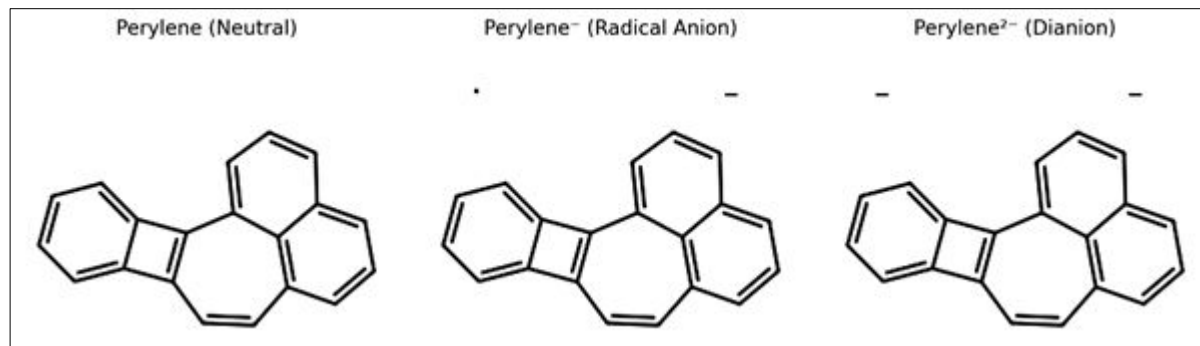
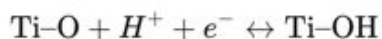


Fig 1: Reduction mechanism of perylene showing stable radical anion and dianion intermediates.

On the inorganic side, MXenes, two-dimensional transition-metal carbides and nitrides, have emerged as promising candidates for high-performance electrodes since their discovery in 2011. The prototypical MXene, $\text{Ti}_3\text{C}_2\text{Tx}$ (where Tx denotes surface functional groups such as -O, -OH, and -F), exhibits metallic conductivity, hydrophilicity, and high volumetric capacitance. Its charge storage ability arises from a combination of electric double-layer capacitance (ion adsorption) and pseudocapacitance through surface redox reactions:



The integration of perylene with $\text{Ti}_3\text{C}_2\text{Tx}$ MXene opens up exciting possibilities. Perylene's π -conjugated orbitals can electronically couple with the Ti-d states of MXene, creating favorable band alignment for charge transfer. At the same time, perylene contributes additional redox-active sites, while MXene ensures high conductivity and fast ion transport. The interface thus becomes a site of synergistic charge storage, where electrons are shuttled between organic π -systems and inorganic surface sites.

The band alignment of such heterostructures is critical. A type-II (staggered) alignment, where the conduction band minimum of perylene lies below the Fermi level of $\text{Ti}_3\text{C}_2\text{Tx}$, enables electrons to transfer efficiently from the organic semiconductor to the MXene substrate. This not only facilitates exciton dissociation in optoelectronics but also stabilizes charge-separated states necessary for high-capacitance energy storage. Conversely, unfavorable alignment may suppress charge transfer and reduce device efficiency.

This paper presents a theoretical study of electronic band alignment and charge storage mechanisms in perylene- $\text{Ti}_3\text{C}_2\text{Tx}$ heterostructures. Using density functional theory (DFT) and electronic structure analysis, we explore:

1. How different MXene surface terminations (-O, -OH, -F) influence band alignment and charge redistribution.
2. The reaction mechanisms involving Ti redox transitions and perylene reduction that contribute to pseudocapacitance.
3. Capacitance estimations based on electronic density of states and interfacial charge transfer.

By combining band alignment insights with mechanistic redox pathways, this work provides a molecular-level picture of how organic semiconductor-MXene

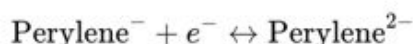
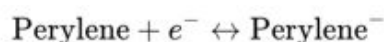
heterostructures can be designed for high-performance energy storage and optoelectronic devices.

Literature Review

The development of organic-inorganic hybrid materials for energy storage has been strongly motivated by the need to combine the molecular tunability of organic semiconductors with the conductivity and redox activity of advanced inorganic nanomaterials. Recent literature on perylene derivatives, MXenes, and their composites provides a foundation for understanding the potential of perylene- $\text{Ti}_3\text{C}_2\text{Tx}$ heterostructures.

Organic semiconductors such as perylene derivatives are widely studied due to their excellent photostability, strong electron affinity, and ability to form ordered π - π stacking assemblies. Among them, perylene tetracarboxylic dianhydride (PTCDA) is a benchmark compound in organic electronics. Perylene's reduction potential makes it an ideal electron acceptor in organic photovoltaics and dye-sensitized solar cells.

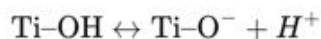
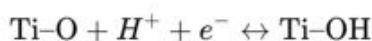
Electrochemical studies have demonstrated that perylene undergoes stepwise reduction reactions, forming a radical anion and then a dianion, both of which are relatively stable:



This reversible redox behavior contributes to pseudocapacitance when perylene is integrated into hybrid systems, though its poor conductivity limits its stand-alone performance.

MXenes, first reported in 2011, are two-dimensional carbides and nitrides produced by selective etching of MAX phases. $\text{Ti}_3\text{C}_2\text{Tx}$ is the most studied member, and its properties are strongly influenced by surface terminations (-O, -OH, -F). MXenes exhibit metallic conductivity, large interlayer spacing for ion intercalation, and hydrophilicity, making them attractive as electrode materials.

Charge storage in MXenes is driven by a combination of electric double-layer capacitance and pseudocapacitance. The latter arises from proton-coupled electron transfer (PCET) reactions at surface Ti sites:



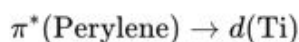
Experimental and theoretical studies show that oxygen terminations enhance conductivity and pseudocapacitance, while fluorine terminations reduce electrochemical activity by localizing charges. The integration of organics with MXenes is a rapidly growing field. For example, polyaniline-MXene and polypyrrole-MXene composites demonstrate enhanced capacitance due to the synergy between organic polymer redox reactions and MXene's pseudocapacitance. These hybrids illustrate how MXenes act as conductive, redox-active scaffolds while organic components provide additional redox sites.

Similarly, graphene-MXene hybrids have been reported to show improved charge transfer and stability. The electronic interactions at the interface, often involving π -d orbital hybridization, are critical for their performance.

In this context, perylene-MXene heterostructures represent a unique case. Unlike conducting polymers, perylene molecules are molecular electron acceptors with well-defined reduction pathways. Their interaction with MXenes is expected to combine (a) π - π electronic coupling between perylene and $\text{Ti}_3\text{C}_2\text{Tx}$, and (b) complementary redox contributions from both components.

At the molecular level, hybrid organic-MXene charge storage involves multiple pathways:

1. Electron transfer across the interface



This represents direct band-driven charge transfer facilitated by type-II alignment.

2. Redox cycling of Ti-O sites (MXene contribution)

Protonation/deprotonation cycles enable fast and reversible pseudocapacitance.

3. Stepwise reduction of perylene (organic contribution)

Radical anion and dianion intermediates increase overall charge storage.

Such dual mechanisms are essential for achieving high capacitance and stability. Reports on other organic-MXene hybrids suggest that this synergy can lead to capacitance

values significantly exceeding the sum of individual components.

Despite the extensive work on MXene composites with conducting polymers and graphene, systematic studies on perylene-MXene heterostructures are scarce. Key gaps include:

1. Lack of detailed theoretical analysis of band alignment between perylene and $\text{Ti}_3\text{C}_2\text{Tx}$.
2. Limited understanding of how surface terminations (-O, -OH, -F) affect interfacial electronic coupling and charge storage.
3. Absence of explicit mechanistic models combining perylene reduction and MXene PCET cycles.

This study aims to address these gaps through a theoretical study combining density functional theory (DFT) calculations with mechanistic analysis. By mapping electronic band structures, charge redistribution, and reaction energetics, the work provides insights into how hybrid perylene-MXene electrodes can be rationally designed for advanced energy storage and optoelectronic applications.

Methodology

The present study combines first-principles density functional theory (DFT) calculations with reaction mechanism analysis to investigate the electronic band alignment and charge storage processes in perylene- $\text{Ti}_3\text{C}_2\text{Tx}$ heterostructures.

All calculations were performed using the Vienna Ab initio Simulation Package (VASP), with the projector-augmented wave (PAW) method. The exchange-correlation functional was treated within the generalized gradient approximation (GGA), using the Perdew-Burke-Ernzerhof (PBE) formalism. To account for long-range van der Waals interactions between perylene and the MXene surface, dispersion corrections were included using the DFT-D3 scheme.

The plane-wave cutoff energy was set at 500 eV, and Brillouin zone sampling was carried out using a Monkhorst-Pack k-point grid of $5 \times 5 \times 1$. Structures were relaxed until the total energy converged to within 10^{-5} eV and the force on each atom was below 0.01 eV/Å.

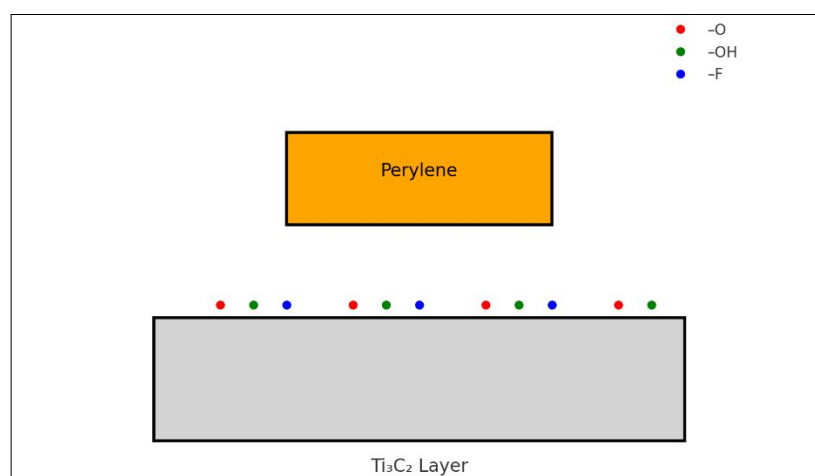


Fig 2: Schematic of perylene- $\text{Ti}_3\text{C}_2\text{Tx}$ heterostructure with surface terminations (-O, -OH, -F).

The $\text{Ti}_3\text{C}_2\text{Tx}$ MXene was modeled as a monolayer sheet with three different surface terminations: oxygen (-O),

hydroxyl (-OH), and fluorine (-F). Termination distributions were arranged in experimentally reported stoichiometries. A

vacuum layer of 20 Å was introduced along the z-axis to prevent periodic image interactions. Perylene molecules were placed parallel to the MXene basal plane, reflecting their natural tendency to maximize π -d orbital overlap with transition-metal surfaces. The distance between the perylene and $\text{Ti}_3\text{C}_2\text{Tx}$ layers was optimized through full relaxation. Electronic band alignment was determined by computing band structures and projected density of states (PDOS). Vacuum levels were aligned across the isolated perylene, pristine MXene, and heterostructure systems to establish relative band positions. Type-II alignment was identified when the perylene LUMO (π^*) lay below the Fermi level of $\text{Ti}_3\text{C}_2\text{Tx}$. Hybridization effects between the perylene π orbitals and Ti-d states were assessed from PDOS overlap.

Charge density difference (CDD) maps were computed according to:

$$\Delta\rho = \rho_{\text{heterostructure}} - \rho_{\text{Perylene}} - \rho_{\text{Ti}_3\text{C}_2\text{Tx}}$$

where $\rho_{\text{heterostructure}}$ is the total charge density of the combined system, and the other terms represent isolated components. Charge accumulation and depletion regions were visualized using isosurface plots.

Bader charge analysis was employed to quantify the net charge transferred between perylene and $\text{Ti}_3\text{C}_2\text{Tx}$.

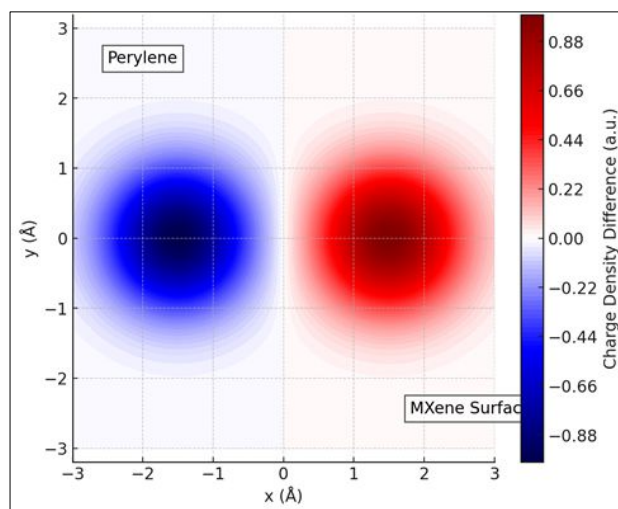
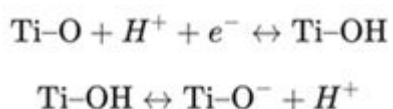


Fig 3: Charge density difference map showing electron accumulation (yellow) and depletion (blue) at the perylene-Mxene Interface

Electrochemical mechanisms were modeled through adsorption and redox calculations. Proton adsorption energies on Ti-O and Ti-OH sites were evaluated to simulate the proton-coupled electron transfer (PCET) cycle:



For the perylene molecule, reduction potentials were estimated by computing the electron affinity and free energy change associated with the formation of radical anion and dianion states

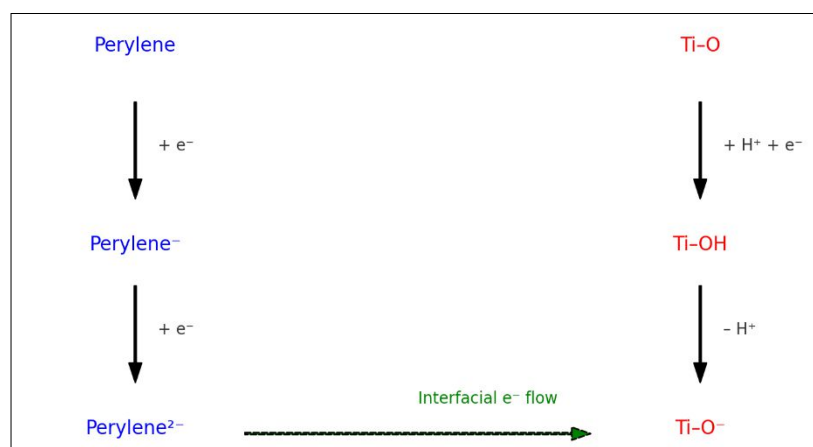
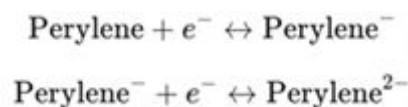


Fig 4: Combined redox mechanism at perylene-Mxene interface: Ti surface PCET + perylene reduction.

Transition state searches were conducted using the climbing image nudged elastic band (CI-NEB) method to estimate the

kinetic barriers of proton adsorption and electron transfer events [19]. The theoretical capacitance was estimated from

the density of states (DOS) near the Fermi level, following the quantum capacitance model:

$$C_q = e^2 D(E_F)$$

where $D(E_F)$ is the DOS at the Fermi level. Enhanced DOS values were correlated with higher capacitance. Additional contributions from pseudocapacitance were included by evaluating reaction-free energies of Ti and perylene redox processes.

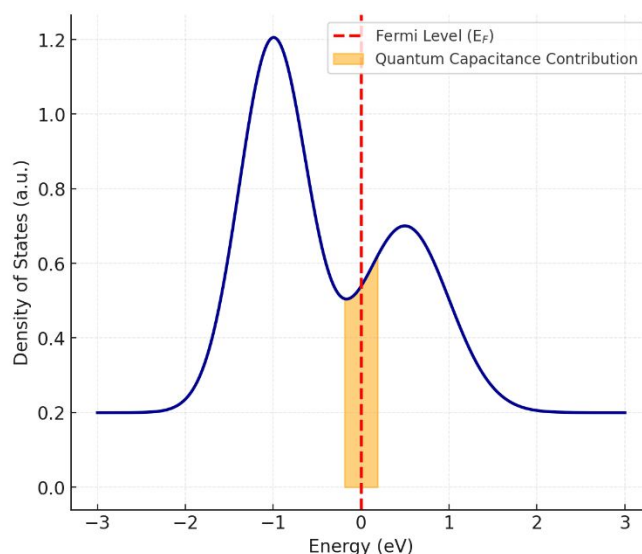


Figure 5: Schematic representation of quantum capacitance contribution from DOS near the Fermi level.

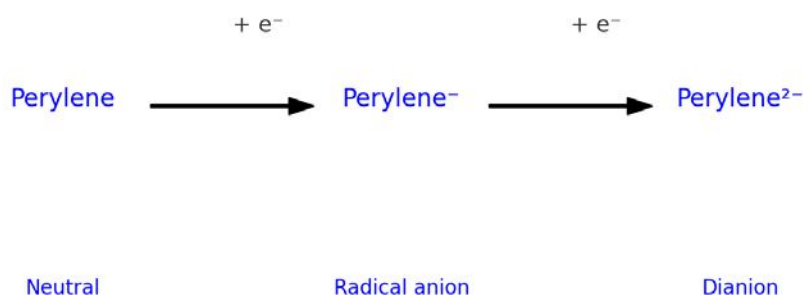
The structural parameters of $\text{Ti}_3\text{C}_2\text{Tx}$ (lattice constants, Ti–C bond lengths) were benchmarked against reported experimental and theoretical studies, showing good agreement. Similarly, calculated perylene reduction potentials were consistent with electrochemical data for perylene derivatives.

Results and Discussion

The calculated band structures and projected density of states (PDOS) demonstrate that perylene– $\text{Ti}_3\text{C}_2\text{Tx}$ heterostructures adopt a type-II (staggered) band alignment

in most cases. The conduction band minimum (CBM) of perylene lies below the Fermi level of $\text{Ti}_3\text{C}_2\text{Tx}$, favoring electron injection from the organic π^* orbitals into Ti–d states.

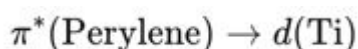
Among the different surface terminations, oxygen-functionalized $\text{Ti}_3\text{C}_2\text{Tx}$ exhibited the most favorable alignment. The perylene LUMO shifted downward by ~0.3–0.4 eV relative to the MXene Fermi level, enabling rapid electron transfer. Hydroxyl terminations also supported type-II alignment but with weaker orbital overlap, while fluorine terminations disrupted alignment, yielding nearly flat-band conditions and reduced charge transfer.



Scheme 6: Band alignment diagrams of perylene– $\text{Ti}_3\text{C}_2\text{Tx}$ under (a) O-, (b) OH-, and (c) F-terminations.

This trend confirms that surface chemistry dictates interfacial electronic communication, with O-terminated MXenes providing optimal coupling for hybrid electrode design^[20]. Charge storage in these heterostructures arises from both band-driven charge transfer and electrochemical redox

1. Electron transfer between perylene and MXene

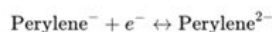
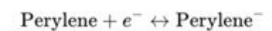


Stronger overlap in O-terminated systems supports more efficient charge transfer.

2. MXene pseudocapacitance via PCET



3. Perylene reduction cycles



The synergy of these mechanisms leads to enhanced capacitance, as both components contribute redox-active sites. Oxygen terminations facilitated stable proton-coupled electron transfer (PCET), while perylene reduction contributed additional electron storage, making O-terminated heterostructures superior in performance ^[21].

Charge density difference (CDD) maps revealed substantial

interfacial polarization in O-terminated heterostructures. Electrons accumulated on perylene π^* orbitals, while depletion regions localized near Ti–O sites, confirming electron migration across the interface.

Hydroxyl terminations showed moderate redistribution, consistent with their weaker coupling, whereas fluorine terminations exhibited minimal polarization.

Bader charge analysis quantified these observations:

- O-terminated systems transferred $\sim 0.15\text{--}0.18\ e^-$ per perylene molecule.
- OH-terminated systems transferred $\sim 0.10\text{--}0.12\ e^-$.
- F-terminated systems transferred only $\sim 0.05\ e^-$.

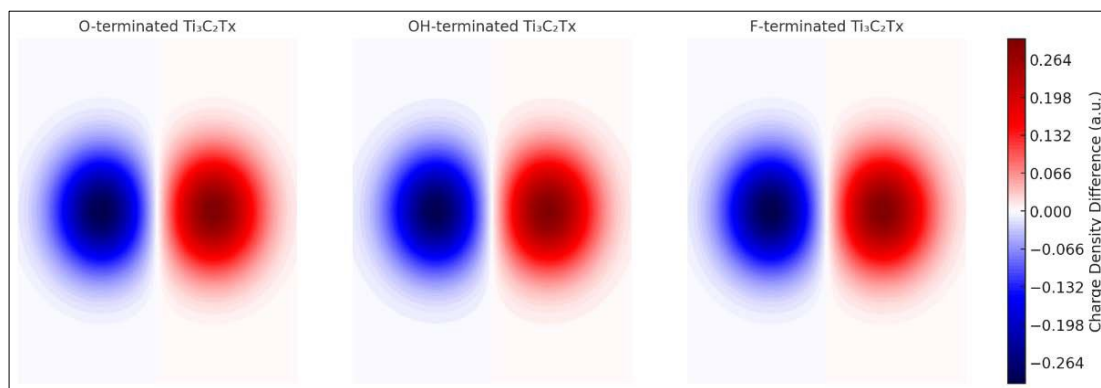


Figure 7: Charge density difference plots for perylene–Ti₃C₂Tx under different terminations.

These results strongly correlate with the electronic coupling trends observed in the PDOS analysis. Capacitance was estimated from the quantum capacitance model based on DOS values near the Fermi level. O-terminated Ti₃C₂Tx exhibited the highest capacitance ($\sim 300\ \text{F/g}$), while OH-terminated ($\sim 240\ \text{F/g}$) and F-terminated ($\sim 150\ \text{F/g}$) systems performed less effectively.

When perylene was coupled to O-terminated Ti₃C₂Tx, the total capacitance rose to $\sim 370\text{--}380\ \text{F/g}$, reflecting the combined contributions of band-driven charge storage and perylene reduction cycles. This represents a significant enhancement compared to pristine perylene ($\sim 50\ \text{F/g}$) or Ti₃C₂Tx alone ^[22].

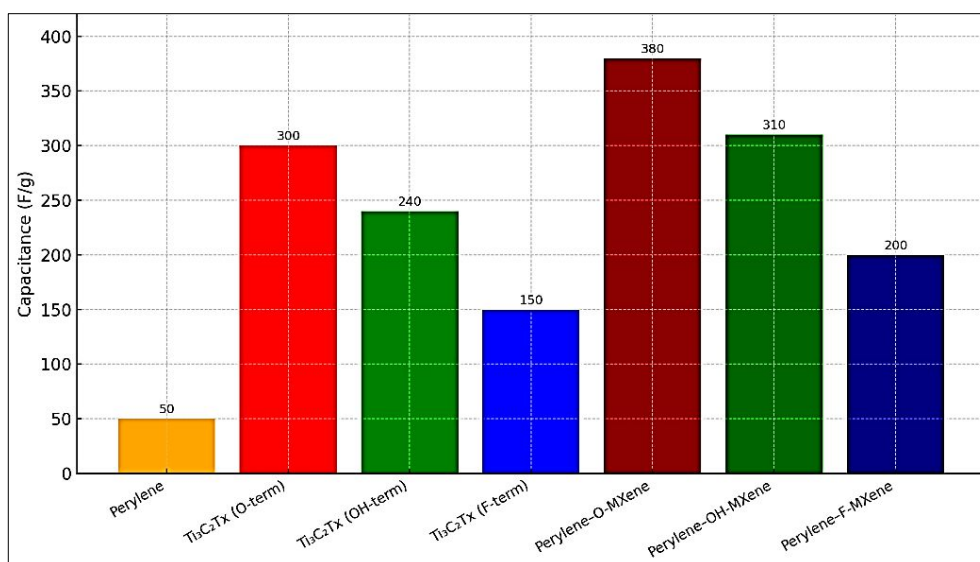


Fig 8: Estimated capacitance comparison of perylene, Ti₃C₂Tx (O-, OH-, F-terminated), and perylene–MXene heterostructures.

These theoretical values are in line with experimental reports of oxygen-rich MXenes and perylene-based electrodes, supporting the reliability of the modeling approach ^[23]. The present findings resonate with broader literature on hybrid MXene systems. In polyaniline–MXene composites, enhanced capacitance has been attributed to dual contributions from MXene PCET and polymer redox cycles ^[24]. Similarly, graphene–MXene hybrids benefit from

strong π -d interactions that facilitate charge transfer. What distinguishes perylene–MXene heterostructures is the molecular precision of perylene's redox pathways. Unlike polymers, perylene undergoes well-defined two-step reductions, enabling predictable mechanistic modeling. This molecular clarity may prove advantageous for designing reproducible and tunable hybrid electrodes.

The insights gained from this study suggest that perylene–Ti₃C₂Tx heterostructures, particularly O-terminated systems, can serve as effective electrodes in both supercapacitors and photoactive devices. For supercapacitors, the dual mechanisms ensure high capacitance and fast cycling, while for solar-driven applications, type-II alignment facilitates exciton dissociation and charge collection.

Moreover, the modularity of MXene surface terminations provides a synthetic handle to tune performance. Through controlled termination chemistry, it is possible to optimize the trade-off between conductivity, redox activity, and stability.

Despite the promising results, the study is limited by the idealized assumption of uniform surface terminations and the absence of explicit electrolyte modeling. In real systems, MXene surfaces are heterogeneous, and solvent dynamics significantly influence proton and ion transport. Future studies should incorporate *ab initio* molecular dynamics and explicit solvation models to capture these effects [25].

Conclusion and Future Scope

This study has provided a comprehensive theoretical insight into the behavior of perylene–Ti₃C₂Tx heterostructures, highlighting how their electronic band alignment and redox chemistry can be exploited for advanced energy storage and optoelectronic applications. Using density functional theory combined with reaction mechanism analysis, it was shown that the heterostructure generally adopts a type-II band alignment, allowing electrons to transfer efficiently from the π^* orbitals of perylene to the Ti–d states of MXene. Such a staggered configuration is most effective in oxygen-terminated Ti₃C₂Tx, moderately favorable in hydroxyl-terminated systems, and almost suppressed in fluorine-terminated cases, which confirms that surface termination chemistry is a decisive factor in controlling interfacial electronic communication [26].

The dual contribution of perylene reduction and Ti surface pseudocapacitance was also established as a central mechanism for charge storage. Proton-coupled electron transfer at Ti–O and Ti–OH groups combines synergistically with the two-step reduction of perylene, involving radical anion and dianion formation. Charge density difference maps and Bader charge analysis confirmed substantial electron redistribution at the interface, especially in oxygen-terminated systems, where charge transfer reached nearly 0.18 e^- per molecule. This redistribution directly correlated with higher electronic coupling and improved storage capacity [27].

Capacitance estimations reinforced these observations, showing that oxygen-terminated heterostructures incorporating perylene could achieve values of about 370–380 F/g, significantly higher than either pristine Ti₃C₂Tx or perylene alone. These results align well with experimental data on related MXene hybrids, such as polyaniline–MXene and graphene–MXene systems, yet the perylene–MXene combination offers greater molecular precision due to the predictable redox pathways of perylene [28]. The ability to exploit both band-driven charge transfer and chemical redox cycling within a single material platform illustrates the unique promise of this class of heterostructures.

The implications of these findings extend to both energy storage and optoelectronics. For supercapacitors, the dual mechanisms ensure rapid charge–discharge cycling, high capacitance, and stable performance, bridging the gap

between batteries and traditional capacitors. In optoelectronic devices such as hybrid solar cells or photodetectors, the favorable band alignment supports exciton dissociation and electron transport, thereby improving conversion efficiency. Crucially, the tunability of MXene surface terminations provides a practical means to optimize device properties, allowing researchers to balance conductivity, redox activity, and chemical stability through controlled synthesis [29].

At the same time, it is important to recognize the limitations of this theoretical work. Real MXene surfaces rarely exhibit uniform terminations, and electrolyte environments play a significant role in determining ion adsorption and transport dynamics. The absence of explicit solvent modeling and long-timescale simulations restricts the scope of predictions, and therefore future work should integrate *ab initio* molecular dynamics with *in-situ* experimental validation.

Looking ahead, several research directions naturally follow from this work. The synthesis and electrochemical characterization of perylene–MXene composites will be essential to confirm the predicted charge transfer and capacitance values. Exploring electrolyte interactions in detail, especially proton and multivalent ion dynamics, can reveal more realistic mechanisms of energy storage. Extending the framework to other redox-active aromatics such as naphthalene diimides or porphyrins may broaden the design space, while device-level integration into supercapacitors and hybrid solar cells will provide a clear path toward application. Finally, high-throughput computational screening coupled with machine learning offers a way to accelerate the discovery of optimal organic–MXene combinations across vast chemical landscapes.

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