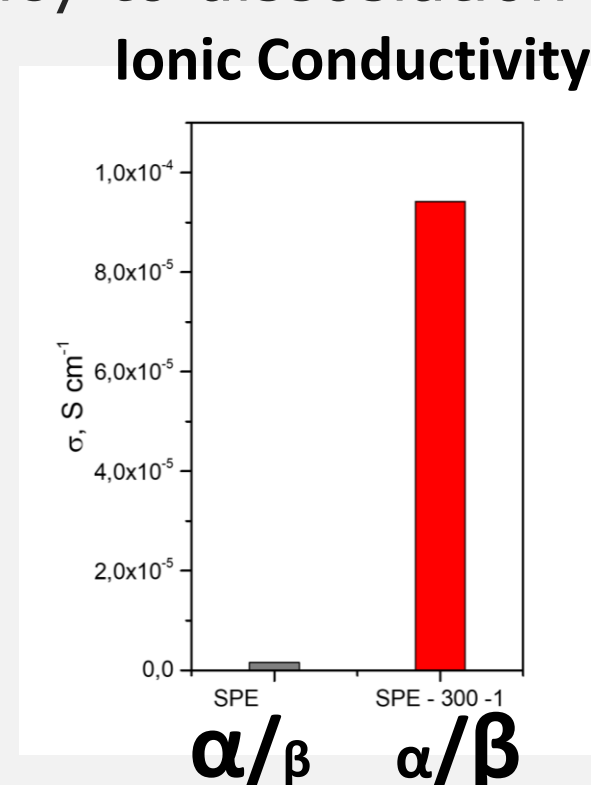
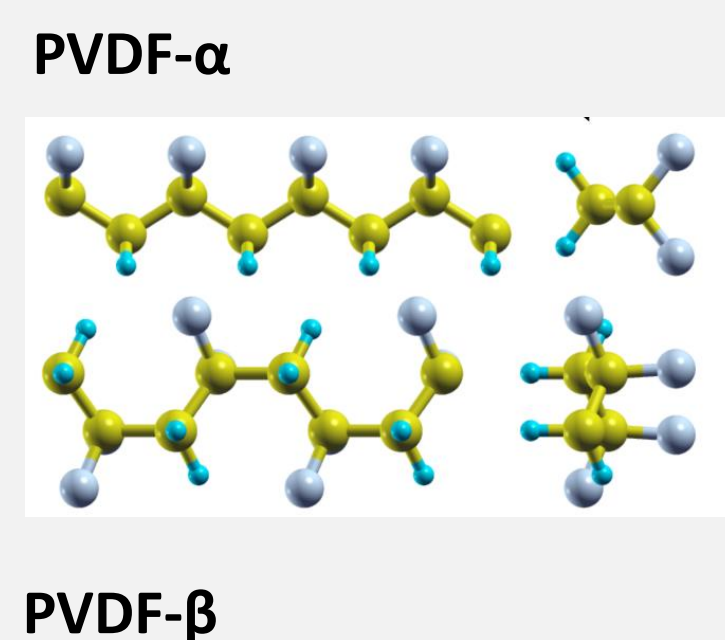
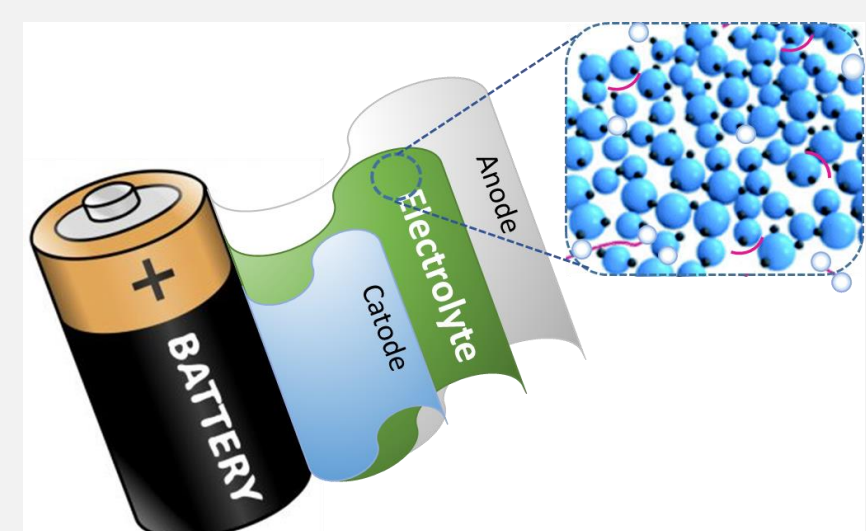


Sylwia Kozdra<sup>a</sup> \*, Michiko Atsumi<sup>b</sup>

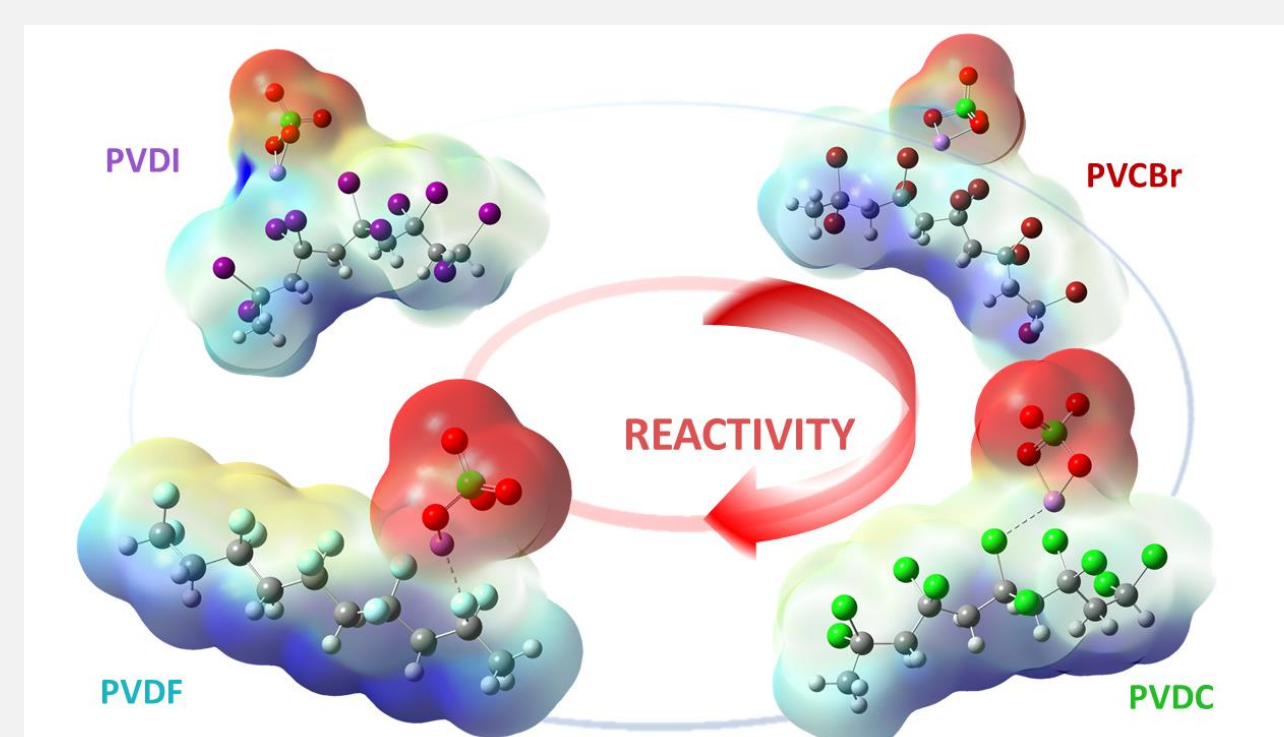
## Energy storage systems with polyhalides

Polyvinylidene halides (PVDX, X = F, Cl, Br, I) have gained attention as potential materials for solid polymer electrolytes, particularly for energy storage applications due to the presence of atoms with increasing electronegativity. PVDF is widely used as a component of solid polymer electrolyte. But the complex structure (range of uniformity of components, crystal form of the polymer matrix) could cause the differences in the properties of the material. PVDF has the polycrystalline structure and the „przewaga” of crystal structure depends of e.g. solvent used during preparation. The crystal forms of PVDF differs in important properties such as polarity or magnetism. The presence of polar on nonpolar crystal structure in polymer electrolyte cause essential differences in properties as an ionic conductivity caused by tendency to dissociation and transport of alkali metal ions.



## Density Function Theory (DFT)

Methods such as Density Function Theory (DFT) can be successfully applied to studying polymers and their composites. Understanding the interactions between polymer chains and lithium salts, such as lithium perchlorate (LiClO<sub>4</sub>), is crucial for optimizing their ion conduction properties and reactivity. Models reflecting the structure of a composite composed of different varieties of polyhalides with the addition of LiClO<sub>4</sub> were optimized and characterized using DFT methods.



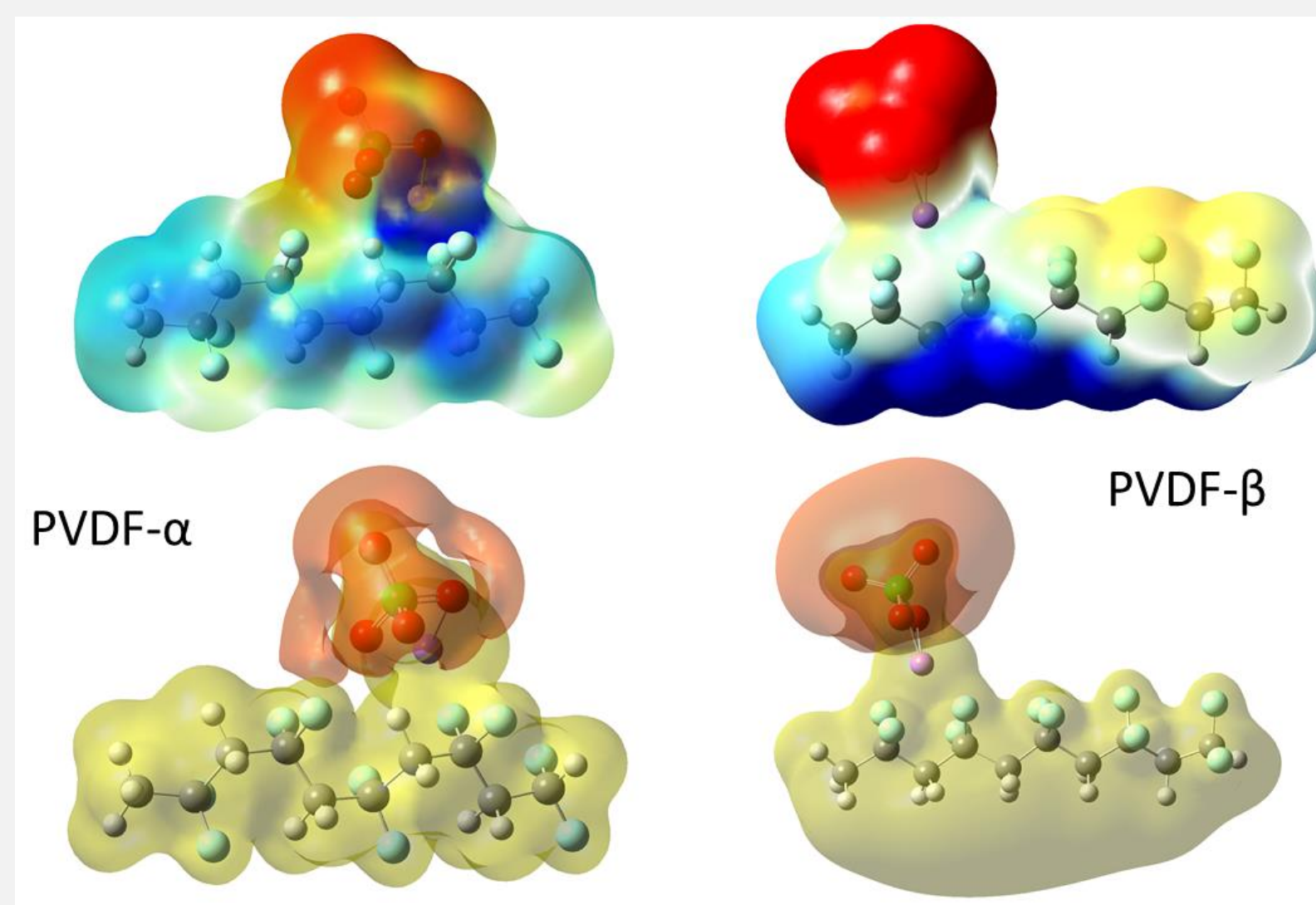
Cluster models for both PVDX-α and PVDX-β were investigated, considering geometry, electrostatic potentials, electron density, Gibbs free energy difference, and the HOMO-LUMO gap.

## Electron density & Electrostatic potential of PVDF, PVDC, PVDB and PVDI α and β crystalline forms

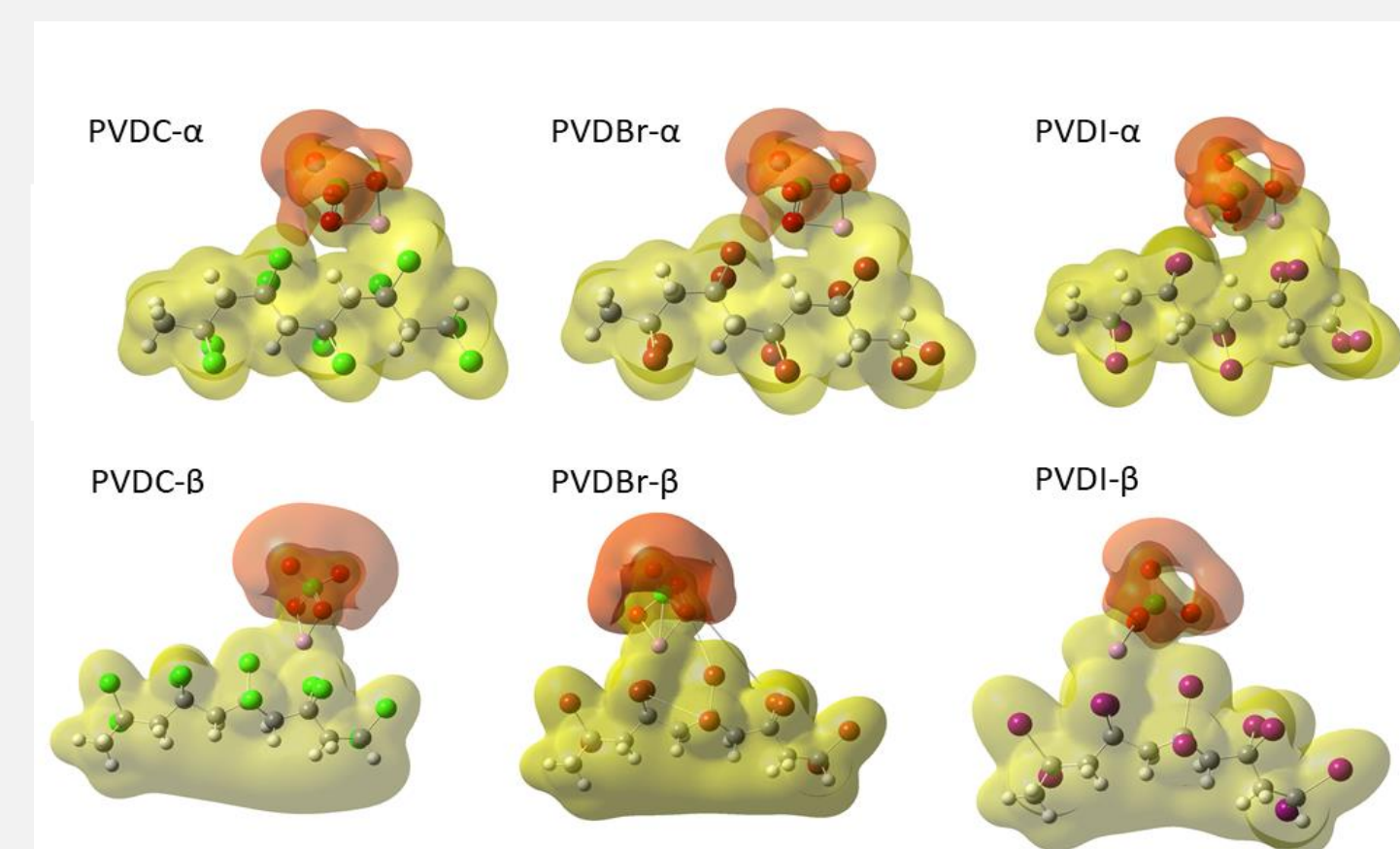
The Electron Density (ED) and Electrostatic Potentials (ESP) serve as valuable descriptors for discerning the sites of electrophilic attack or nucleophilic reactions. ESP analysis facilitates the identification of electron-donor and electron-acceptor regions, delineated in terms of the interaction energy between the electrons. In the visualization, regions rich in electrons were marked in red, indicating donor areas, while blue regions represent acceptor regions with lower electron density.

For the PVDF-α model, a more pronounced red, electron-rich region was observed near the oxygen atoms, with a smaller blue, electron-poor region near the lithium atom. In contrast, for PVDF-β, larger blue, electron-poor regions were evident along the polymer chain. This visual distinction highlights the variations in electron density and charge distribution between the two conformations of PVDF in the presence of the LiClO<sub>4</sub> molecule. The stronger colour gradient indicates that the optimized PVDF-β model interacts more strongly with LiClO<sub>4</sub>, equalizing the charge distribution than PVDF-α.

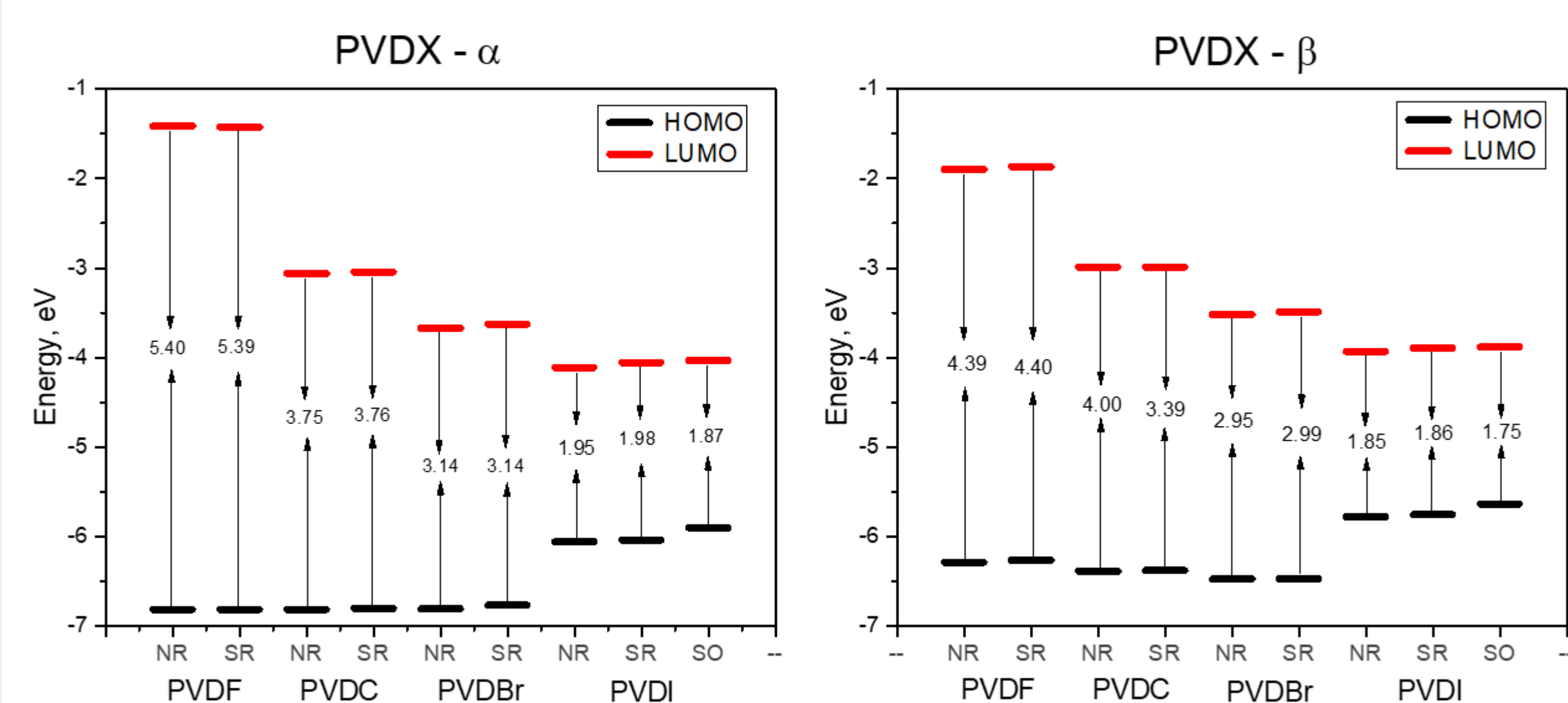
Moreover, for the PVDF-β as well as for PVDC-β model, we can observe the strongest contrast distribution of electrons. For the rest of the models (PVDBr, PVDI) red, rich-in-electrons region was visible near oxygen atoms.



The Electrostatic Potential (ESP) visualization for PVDF-α and β as well as PVDC-α and β revealing a distinct charge environment around the chlorine atom in the α form compared to the β form. This discrepancy has the potential to substantially influence the likelihood of salt dissociation and the release of ions from the perchlorate residue.



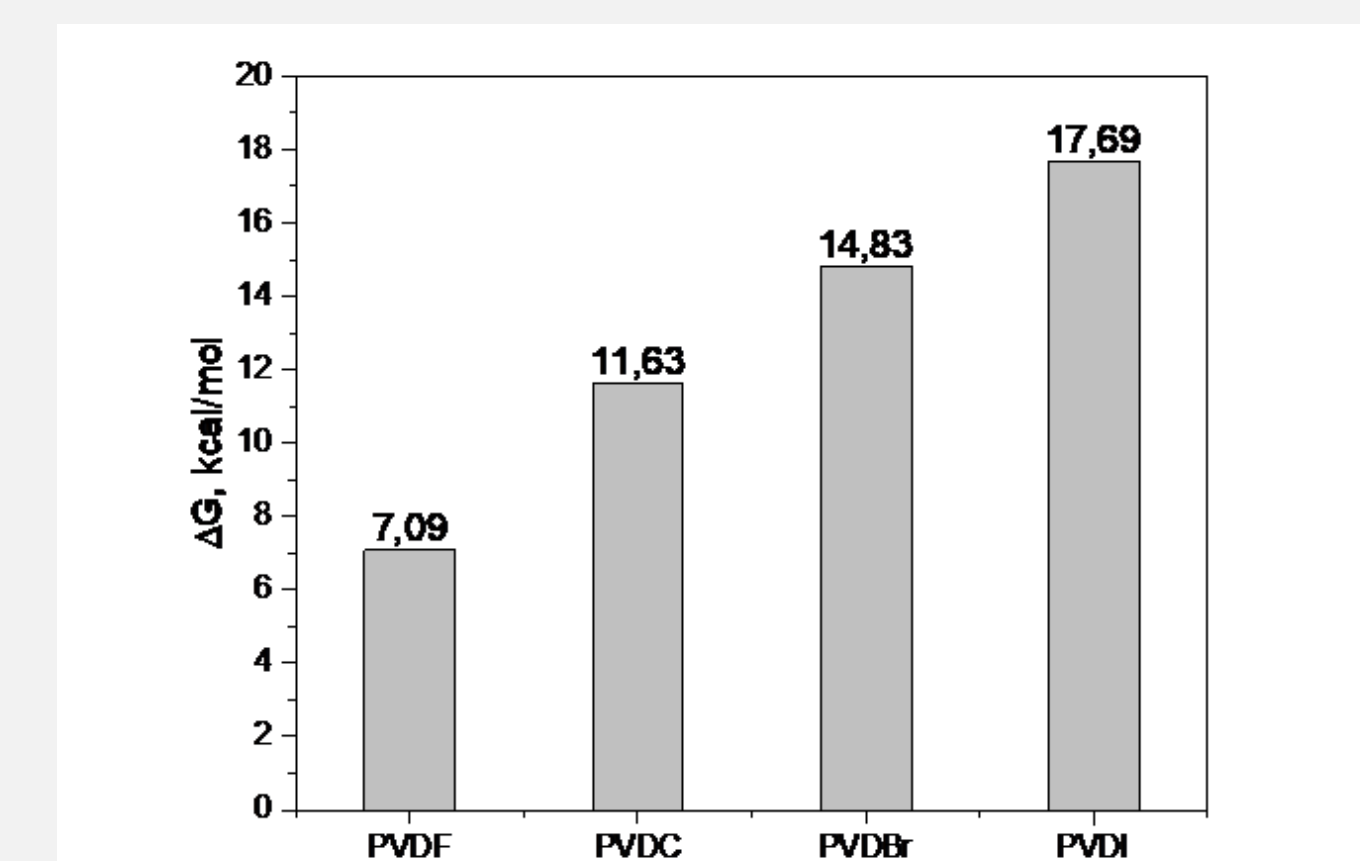
## HOMO LUMO energy band gap



Analyzing the positions of the HOMO and LUMO orbitals for all tested models, it was evident that only in the case of PVDF and PVDC did electron transfer take place, considering the rest of the lithium perchlorate salt and the polymer chain. This shift in orbital location suggested the potential for a reaction between the salt and the polymer, resulting in the dissociation of the salt and releasing a lithium ion that interacted with PVDF. The shape and volume of the LUMO orbital for PVDF β indicated that this phenomenon might be more pronounced for PVDF β than for PVDF α.

## Free Gibbs Energy

The Gibbs free energy (ΔG), has proved to be a useful tool for evaluating the thermodynamic feasibility of reactions in the past. A substantial negative change in free energy during the transition from reactants to products signifies a quantitatively spontaneous (and exothermic) reaction, while a positive value indicates that the reaction demands energy input. The α crystal form predominates and was more stable as confirmed by positive ΔG values. A more positive ΔG correlates with a greater stability disparity between the α and β crystal forms.



## Conclusions

These studies showed that the stability and reactivity of the PVDX polymer chain in the presence of a LiClO<sub>4</sub> salt depends on the type of halogen atom in the chain, but also on the α or β crystalline form considered. Models including PVDF-β and PVDC-β have the potential as components of functional solid polymer electrolytes. Theoretical modeling revealed that the β crystalline forms, especially PVDF-β and PVDC-β, show enhanced electron distribution and a greater tendency to interact with Li<sup>+</sup> ions. This makes them particularly promising for improving ion transport and achieving more efficient charge transfer in solid-state lithium battery systems.

## Affiliations:

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