Strong Impact of Substituent Position in PEAI-Founded Organic Cations to Enable the Efficient and Durable 3D/2D-Constructed Perovskite Solar Cells

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Abstract

The passivation of perovskite solar cells (PSCs) is inevitable to improve their performance and stability. Integrating 2D-forming phenylethylammonium iodide (PEAI) salts for passivation is an emerging strategy due to their hydrophobic character and improved stability in PSCs, although various cations have been implemented. This study investigates the impact of 9 different large organic cations, particularly halogenated with fluorine (F), chlorine (Cl), and bromine (Br) as the substituents at -*ortho* (-*o*), -*meta* (-*m*), and -*para* (-*p*) positioned-PEAI salts (coded as *x*-X-PEAI where *x: o*, *m*, *p* and X:

F, Cl, Br) synthesized using a straightforward method on the passivation of 3D perovskite surfaces and their subsequent effects on device performance and stability. The formation of 2D layers on top of the 3D perovskite was confirmed using X-ray diffraction (XRD) and grazing-incidence wide-angle X-ray scattering (GIWAXS) analyses for all cations, regardless of the nature and position of the halogen. Density functional theory (DFT) analysis was employed to understand the underlying mechanisms behind the observed performance differences. It revealed that m-substituted cations exhibited lower formation energies and higher interfacial dipoles, leading to enhanced device performance compared to their -*ortho* and -*para* counterparts. Among the halogenated PEA+ iodide salts tested, the device treated with *m*-BrPEAI exhibited the highest efficiency of 23.42%, with a high open-circuit voltage (V_{OC}) of 1.13 V and fill factor (FF) of 81.2%. However, considering overall efficiency, stability, and reproducibility, the treatment with *m*-ClPEAI salt yielded the best performance. This comprehensive study contributes to understanding surface passivation in PSCs and offers insights for optimizing device performance through the rational design of large organic cations.

Keywords

3D/2D Perovskite Solar Cells, Substituent and Position Effects, Stability, Large Organic Cations