

Terminal group effects on SAMs packing and perovskite interfacial energetics

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Self-assembled monolayers (SAMs) have emerged as highly efficient hole-selective contacts for inverted perovskite solar cells. [1-3] However, a fundamental understanding of how molecular structure governs monolayer packing and perovskite interfacial energetics remains limited, particularly under air-ambient processing conditions. Here, we report the design and synthesis of two novel triphenylamine-based phosphonic acid SAMs featuring electron-withdrawing (F) and electron-donating (OMe) terminal groups, alongside a neutral analogue, to systematically investigate terminal group effects on interfacial properties. The triphenylamine (TPA) core was selected as a rigid and synthetically accessible scaffold that combines well-established hole-transporting characteristics with broad modularity, enabling straightforward structural functionalization through conventional coupling. Using AFM-IR nanoscale chemical mapping, we demonstrate that terminal group electronics directly dictate SAM packing density and homogeneity, with methoxy substitution yielding the densest and most uniform monolayers. Ultraviolet photoelectron spectroscopy reveals that this enhanced packing is accompanied by favorable interfacial dipole formation and improved energetic alignment with the valence band of FAPbI₃. These interfacial modifications impact perovskite film growth via a two-step deposition process under ambient conditions, leading to compact, void-free films and enhanced interfacial hole extraction, as confirmed by steady-state and time-resolved photoluminescence measurements. In contrast, electron-withdrawing terminal groups result in sparse monolayer coverage, unfavorable energetic offsets, and inefficient charge transfer. This work identifies terminal group engineering within rigid TPA-based SAMs as a key strategy to control molecular packing, interfacial energetics, and perovskite growth, providing molecular-level design guidelines for robust, air-processed perovskite photovoltaics

REFERENCES

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