Supplementary Information:

Sulfur-Fused Perylene Diimide Electron Transport Layers Allow >400 hr Operational Stability of Methylammonium Lead Iodide Photovoltaics

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I. Surface topography of electron transport layers (ETLs)

To reveal the morphology of the ETLs on top of the $MAPbI_3$ layer, we observed surface topographies of the layers with atomic force microscopy (AFM) (Figure S1). Each ETL covers $MAPbI_3$ without major pinholes. Interestingly, **2PDI-0S** and the rest of the **2PDI-nS** series show different features despite small changes in their chemical structures. **2PDI-0S** films have small (200–500 nm) grains, which resemble the morphology of PCBM. In contrast, the samples with annulated sulfur show relatively smooth surfaces without distinctive features from submicron grains. When the number of sulfur increases, the surface of the film starts to undulate in a micrometer order.

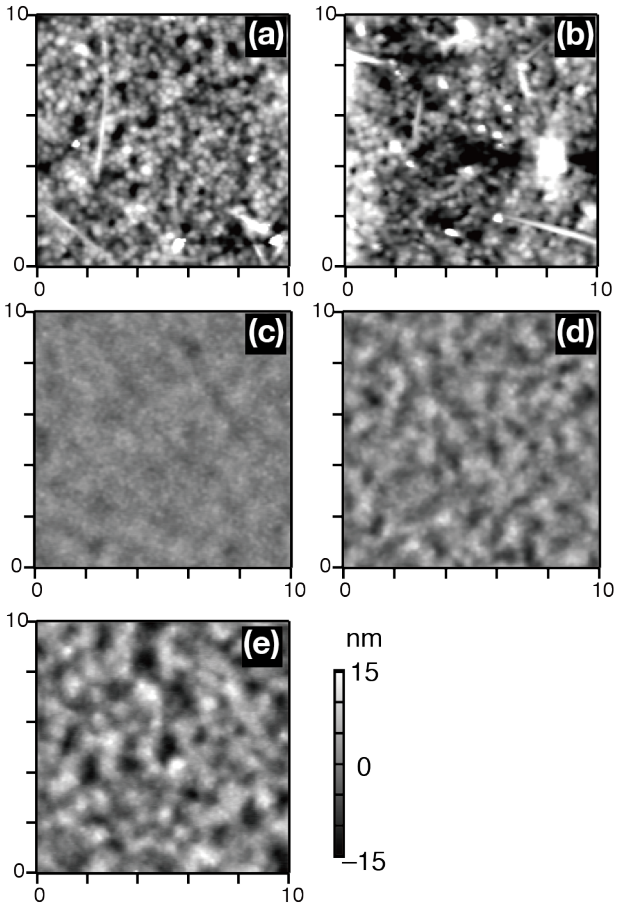

Figure S1. AFM topography images (10 μm x 10 μm) of ETL (a) PCBM, (b) **2PDI-0S**, (c) **2PDI-2S**, (d) **2PDI-3S**, (e) **2PDI-4S** on $MAPbI_3$. The films were not thermally annealed.

II. Characteristics of $MAPbI_3$ solar cells

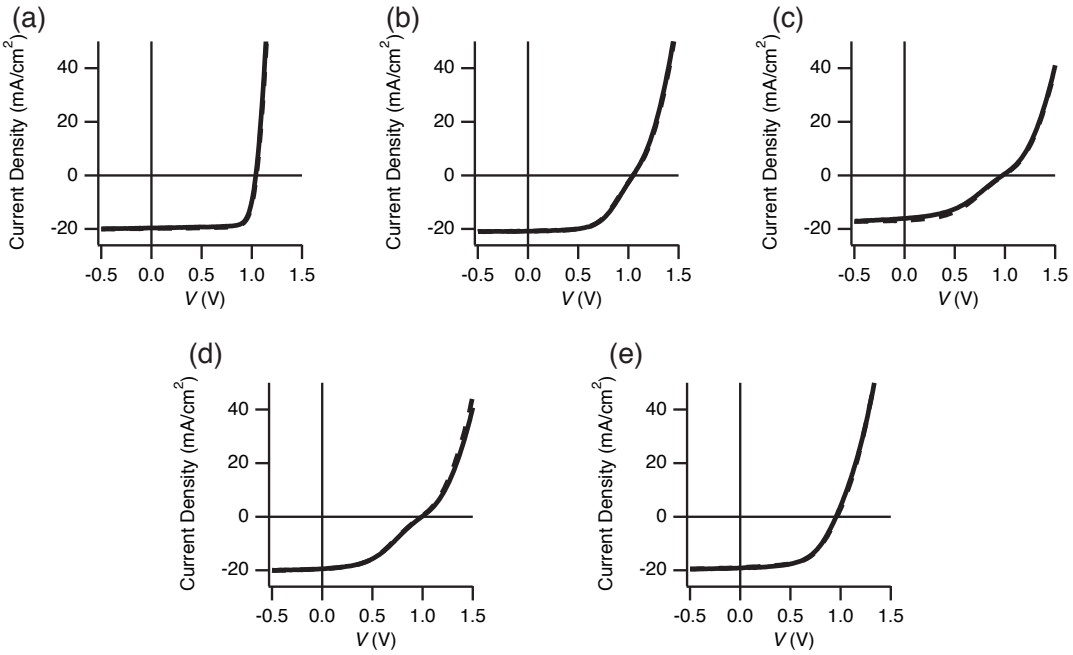

Figure S2. Representative *J–V* characteristics of as-deposited solar cells using (a) PCBM, (b) **2PDI-0S**, (c) **2PDI-2S**, (d) **2PDI-3S**, and (e) **2PDI-4S** as ETL. Solid lines: reverse (1.5 V to –0.5 V) scan, Dashed lines: forward scan.

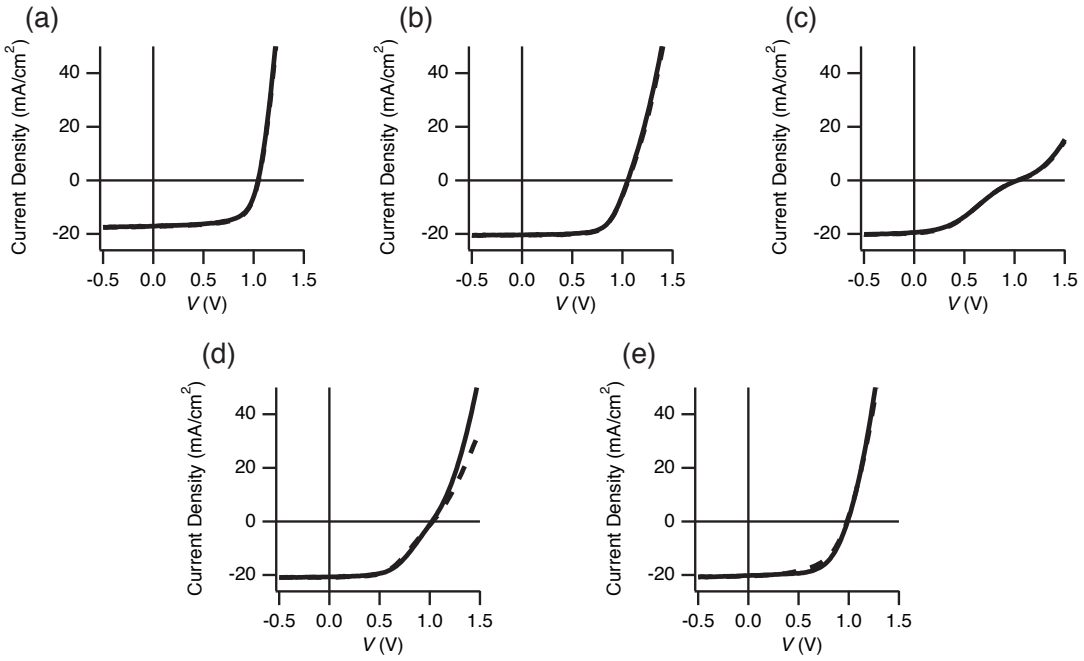

Figure S3. Representative *J*–*V* characteristics of annealed (100 °C, 10 min) device using (a) PCBM, (b) **2PDI-0S**, (c) **2PDI-2S**, (d) **2PDI-3S**, and (e) **2PDI-4S** as ETL. Solid lines: reverse (1.5 V to –0.5 V) scan, Dashed lines: forward scan (mostly overlapped with the solid lines).

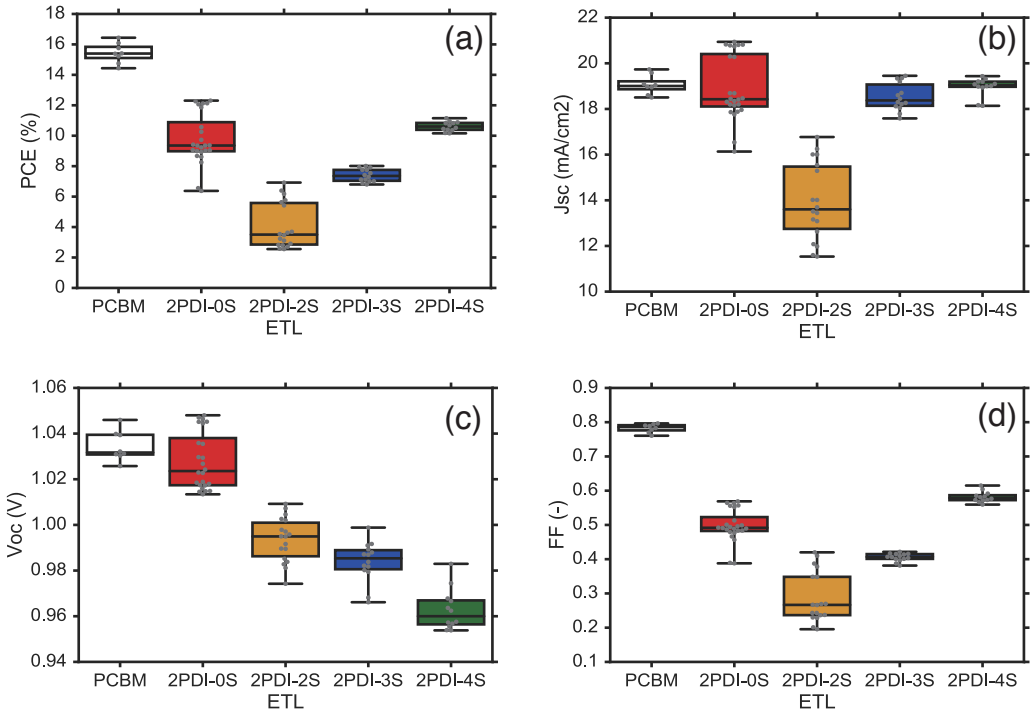

Figure S4. Distribution of device performance characteristics for the devices without thermal annealing. The five lines in the boxplots show 0, 25, 50, 75, and 100 percentiles from the bottom to the top, respectively.

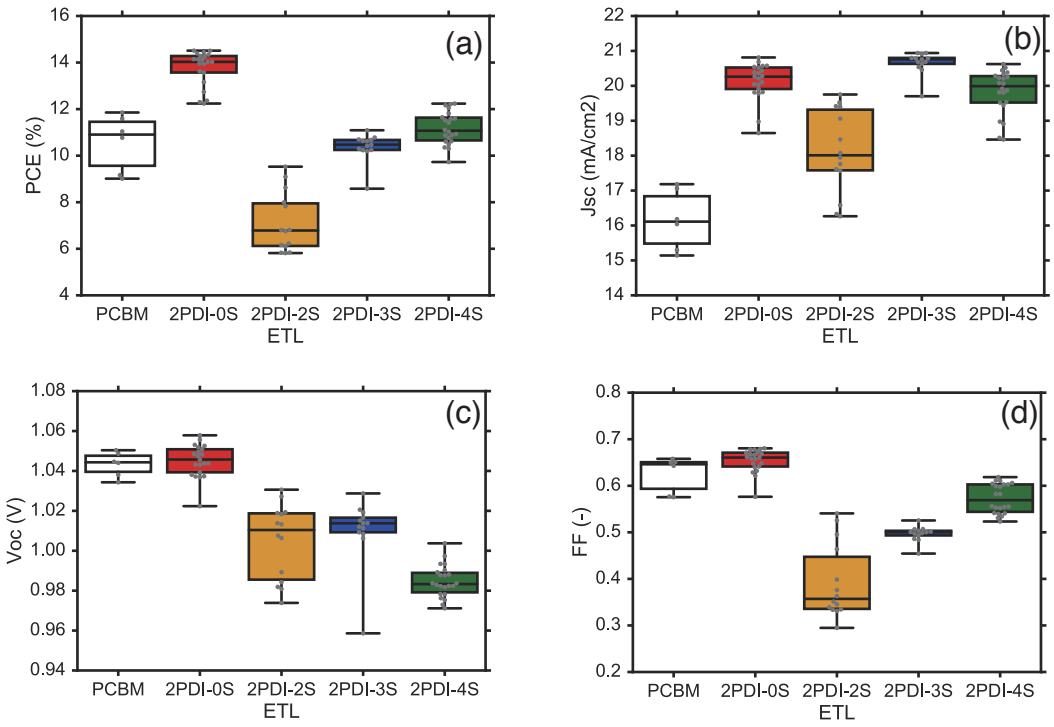

Figure S5. Distribution of device performance characteristics for the devices after a thermal annealing at 100 °C 10 min. The five lines in the boxplots show 0, 25, 50, 75, and 100 percentiles from the bottom to the top, respectively.

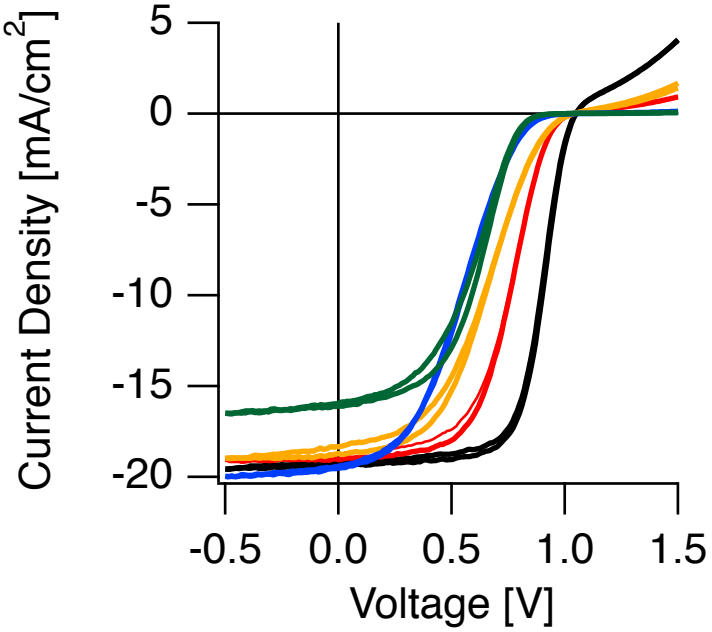

Figure S6. Representative *J–V* characteristics of the devices without an PEIE layer. PCBM (black), **2PDI-0S** (red), **2PDI-2S** (orange), **2PDI-3S** (blue) and **2PDI-4S** (green) as the ETL.

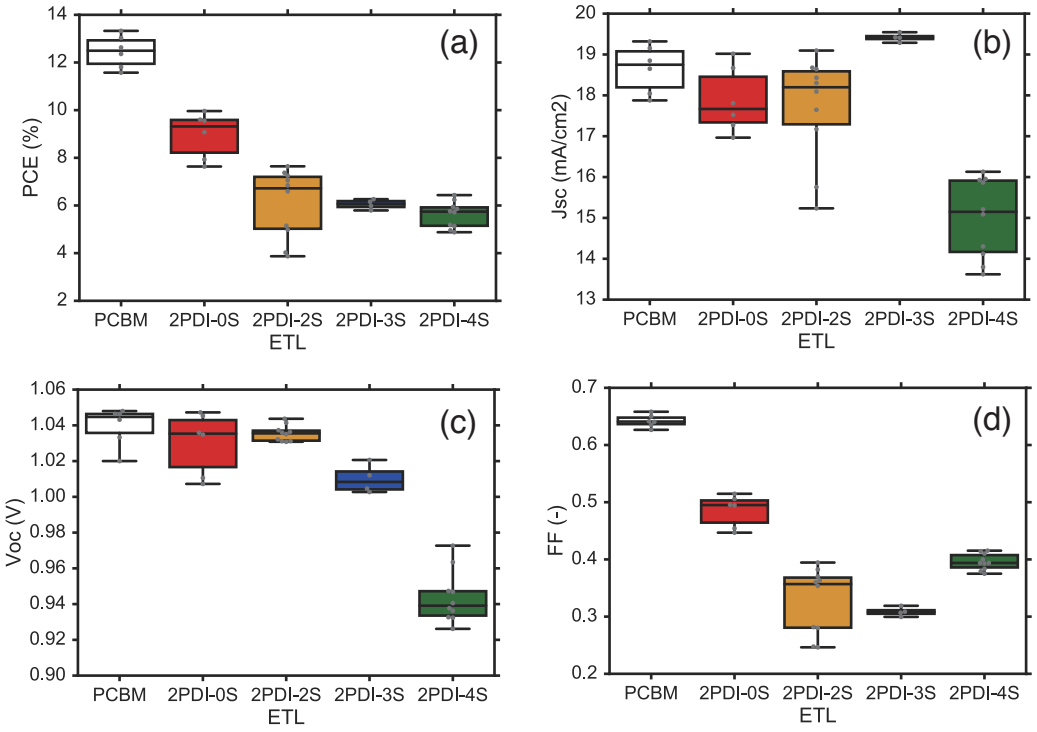

Figure S7. Distribution of device performance characteristics for the devices without PEIE layer. The five lines in the boxplots show 0, 25, 50, 75, and 100 percentiles from the bottom to the top, respectively.

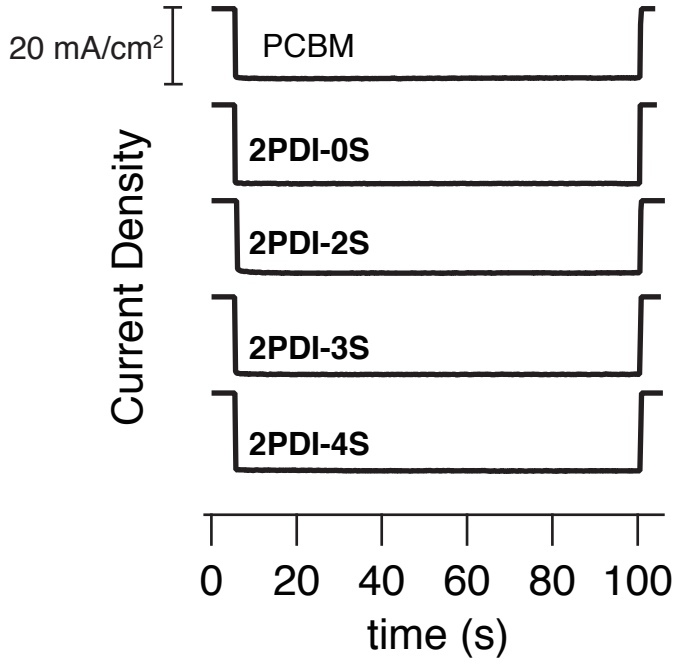

Figure S8. Time-dependent photocurrent, i.e. transient photocurrent (TPC) of the devices under the short-circuit condition. 1 sun illumination was turned on at about 5 s, and off at around 100 s.

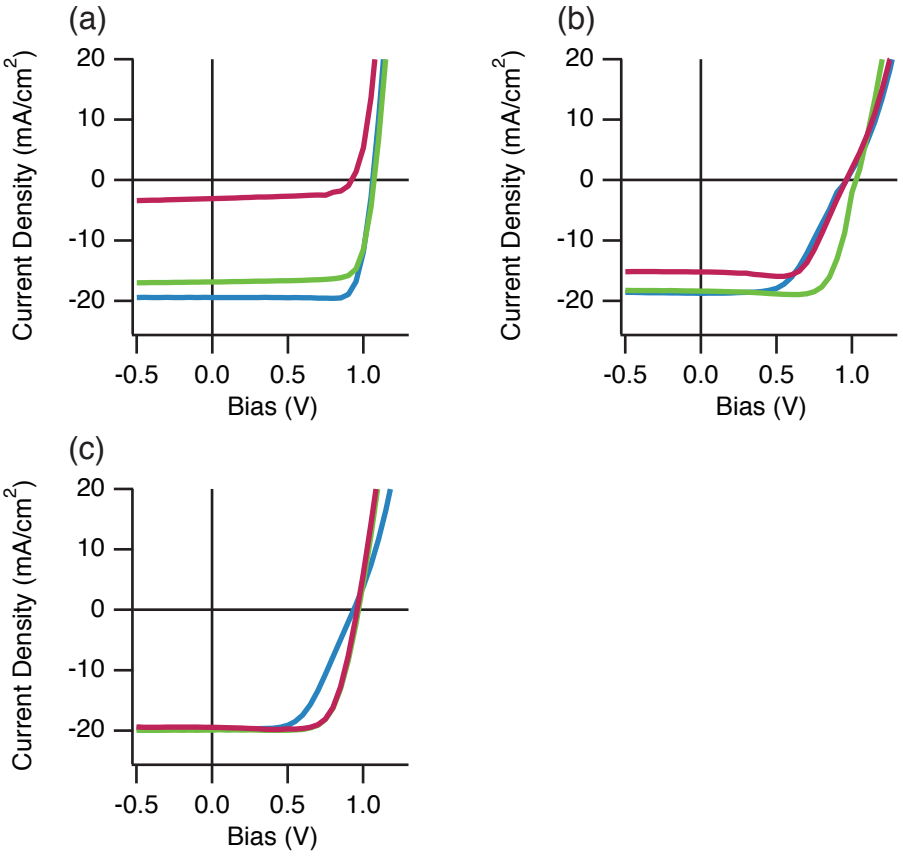

Figure S9. Development of *J*–*V* characteristics of (a) PCBM, (b) **2PDI-0S**, and (c) **2PDI-4S** under light-soaking. Blue: t = 0.1 hr, green: t = 30 hr, and red: t = 285 hr. Note that, for **2PDI-4S**, the characteristics of t = 30 and 285 hr are almost identical.

References

1. W. Becker, Advanced time-correlated single-photon counting techniques. Springer, Berlin, Heidelberg, New York, 2005