

Supporting Information

**Ultralong Perovskite Microrods: One- versus Two-Step
Synthesis and Enhancement of Hole-Transfer During
Light Soaking**

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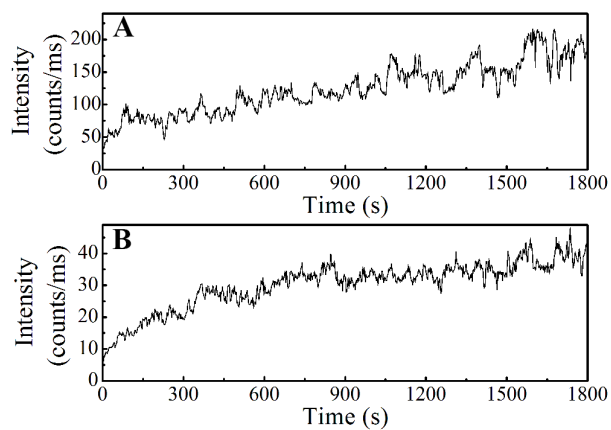


Figure S1. Typical PL intensity trajectories of two randomly selected points on MAPbI₃ perovskite microrods covered by a layer of PMMA. The *EF* for (A) and (B) are 6.6 and 10.3, respectively. Bin-time is 2 s.

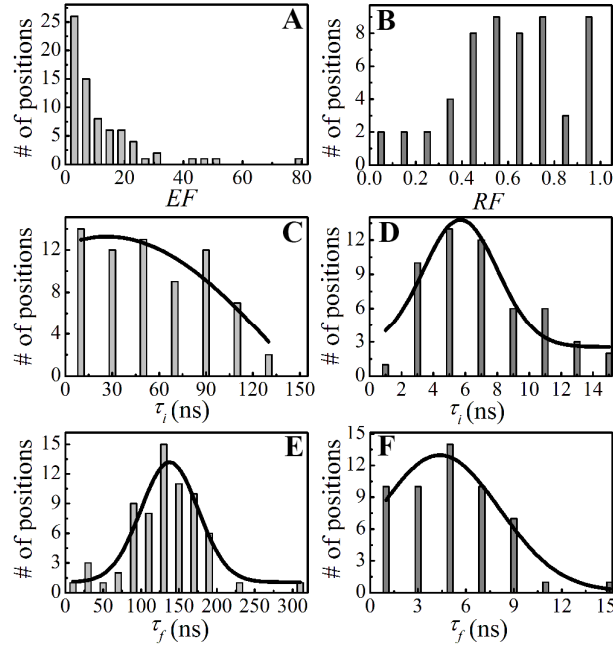


Figure S2. Histograms of the enhancement factor (EF), reduction factor (RF), initial lifetime τ_i (obtained from the monoexponential PL decays constructed from photons between 0 and 2 s) and final lifetime τ_f (obtained from the monoexponential PL decays constructed from photons between 1798 and 1800 s) of several randomly chosen points on single perovskite microrods prepared via the one-step synthesis method in the absence ((A) for EF , (C) for τ_i , (E) for τ_f) and presence ((B) for RF , (D) for τ_i , (F) for τ_f) of spiro-OMeTAD. At the start of measurement, the mean values of τ_i in the absence and presence of spiro-OMeTAD are *ca.* 26.6 (C) and 5.7 ns (D), respectively, which gives rise to $k_{ht} \sim 1.38 \times 10^8 \text{ s}^{-1}$. On the other hand, the hole-transfer rate calculated at the end of the light soaking measurement is $k_{ht} \sim 2.22 \times 10^8 \text{ s}^{-1}$, where the mean values of τ_f in the absence and presence of spiro-OMeTAD are *ca.* 137.7 (E) and 4.4 ns (F), respectively.

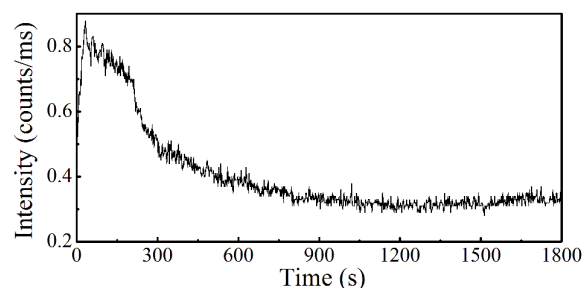


Figure S3. Typical PL intensity trajectory (bin-time = 2 s) of a randomly selected point on an as-prepared MAPbI₃ perovskite film in the presence of a layer of spiro-OMeTAD.

Video captions:

Video S1. Time-lapse microscopy images of the growth evolution of PbI₂ microrods prepared by evaporating a droplet of 1 wt% PbI₂/DMF solution.

Video S2. Time-lapse microscopy images of the growth evolution of PbI₂ microrods prepared by evaporating a droplet of 5 wt% PbI₂/DMF solution.

Video S3. Time-lapse microscopy images of the growth evolution of MAPbI₃ perovskite microrods prepared *via* the one-step synthesis method. The growth of the perovskite is recorded by illuminating the sample with white light for the first 146 s. The sample is then illuminated with laser light of excitation wavelength = 633 nm, and at $t = 9$ min 28 s, PL from the perovskite is observed. The recordings from $t = 2$ min 40 s to 9 min are not shown.