Electronic supplementary information

Terpyridine-zinc(II) coordination nanosheets as modulators of perovskite crystallization to enhance solar cell efficiency

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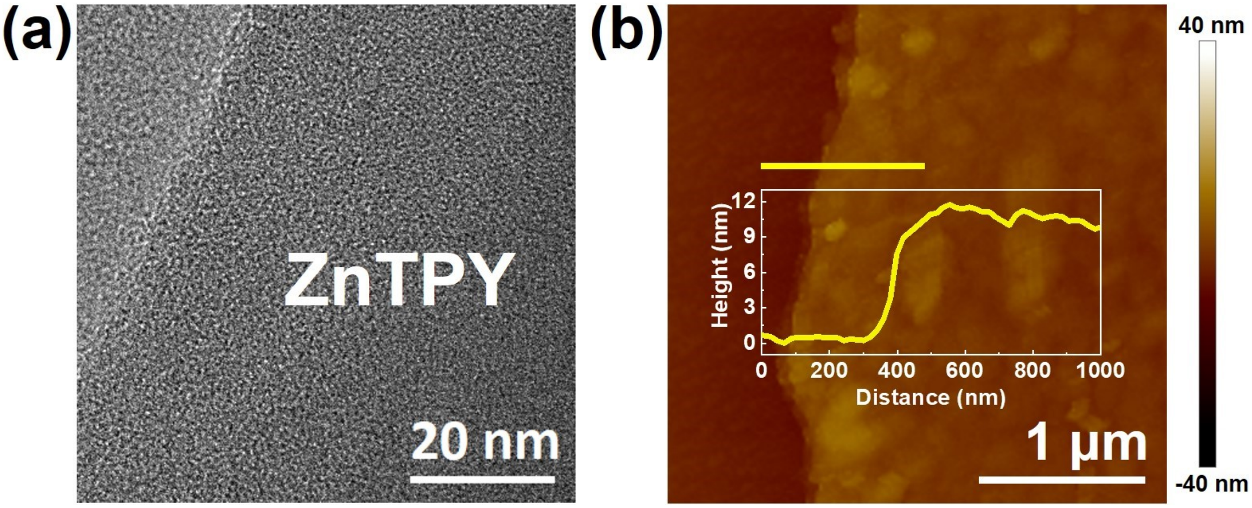
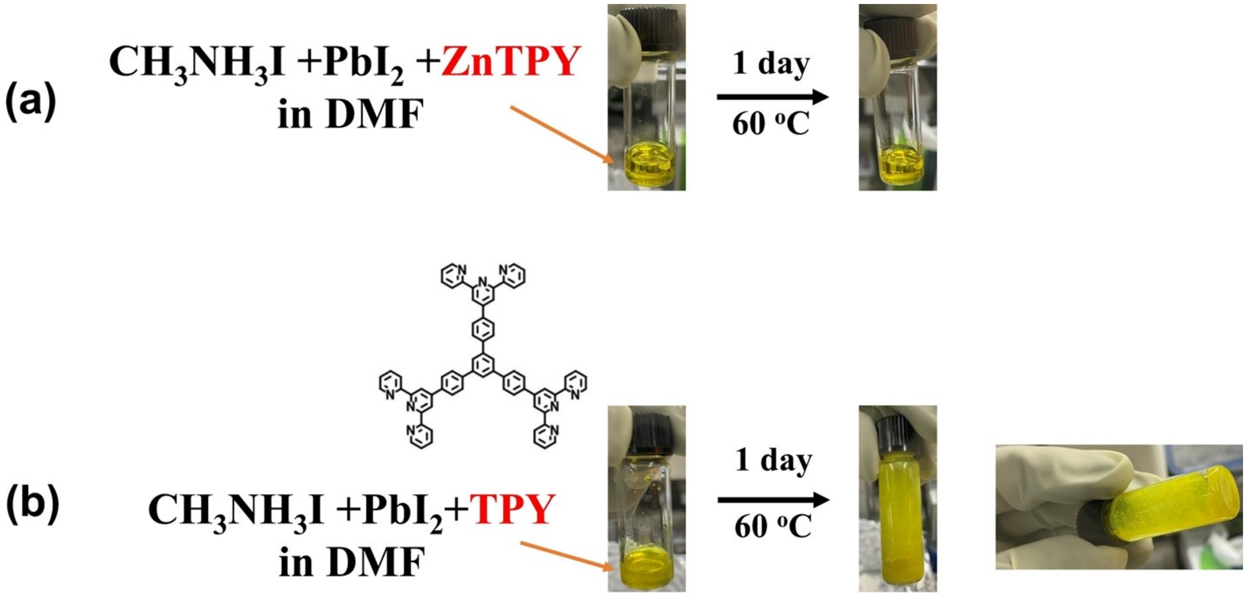
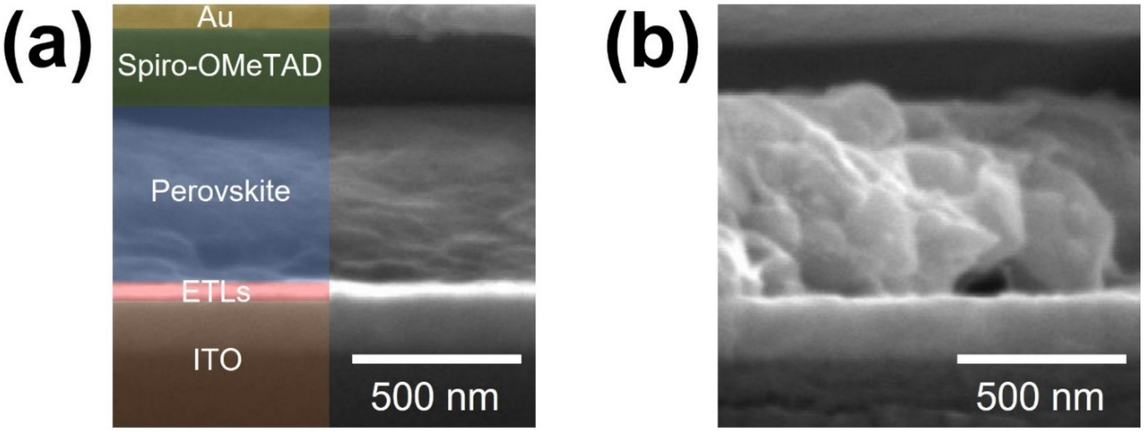
Supplementary Figures



Supplementary Fig. 1 | Characterization of the ZnTPY nanosheet before crushing. (a) Top-view TEM image of the ZnTPY nanosheet. **(b)** AFM image and the corresponding depth profile of ZnTPY nanosheet on a silicon wafer substrate.



Supplementary Fig. 2 | Strong interaction of the TPY ligand with perovskite precursors. Preparation process of perovskite precursor solution **(a)** with ZnTPY CONASHs and **(b)** with TPY ligands.



Supplementary Fig. 3 | Cross-sectional morphology of the ZnTPY-modified PSC. Cross-sectional SEM images of **(a)** ITO/ETLs/$CH_3NH_3PbI_3$ perovskite+ZnTPY/Spiro-OMeTAD/Au and **(b)** ITO/ETLs/$CH_3NH_3PbI_3$ perovskite/Spiro-OMeTAD/Au structures.

Experimental details

PSC fabrication. All PSC devices preparation processes are the same as in our previous article.[1] The electron transporting SnO_2 dispersion (Alfa Aesar) was diluted to 2.67 wt% with deionized H_2O. The aqueous solution was spin-coated on the O_2 plasma cleaned-ITO glass at 3000 rpm for 30 s. The ITO coated with SnO_2 was then annealed at 150°C for 30 min and transferred to a glove box filled with N_2 for subsequent experiments. C_{60} pyrrolidino triglyceride (CPTA, Sigma-Aldrich, 97%) dispersed in dimethylformamide (DMF) at a concentration of 2 mg/ml. The ITO/SnO_2 substrate was spin-coated with CPTA/DMF solution at 4000 rpm for 30 s and annealed at 140°C for 10 min to obtain the second electron transport layer. Immediately afterwards, 1 ml of pristine perovskite precursor solution [1.25 M of DMF with a molar ratio of 1:1 of PbI_2 (Alfa Aesar, 99.9985%) to CH_3NH_3I (Xi'an Polymer Light Technologies, ≥99.5%)] was added into a beaker with 5 mg of urea (Alfa Aesar, 98+%) and stirred at 60 °C for 8 h. The ZnTPY-contained perovskite solution was added in a 100:1 weight ratio of pristine perovskite solution to ZnTPY solution (10% dispersion of ZnTPY in DMF). Then, the precursor solution with or with the addition of ZnTPY CONASHs was spin-coated on the ITO/SnO_2/CPTA substrate at 5000 rpm for 30 s, with chlorobenzene (CB) antisolvent treatment 8 s after the spin-coating process began. After that, the film was annealed at 100 °C for 10 min. Additional, the hole transporting solution was obtained by combining 1 ml of 72.3 mg/ml of f 2,2′,7,7′-tetrakis-(N,N-di-p-methoxyphenylamine)9,9′-spirobifluorene (Spiro-OMeTAD, Borun Chemicals, 99.7%) in CB, 28.8 µl of 4-tert-butylpyridine (Sigma-Aldrich, 96%) and 17.5 µl of 520 mg/ml of lithium bis(trifluoromethylsulfonyl)imide (Sigma- Aldrich, 99.9%) in acetonitrile as a stock solution. The hole transport layer was spin-coated at 2000 rpm for 30 s from the Spiro-OMeTAD solution, followed by thermal evaporation of a 100 nm Au cathode.

Characterization and measurements. X-ray photoelectron spectroscopy (XPS) experiments was recorded using the VG Scientific SIGMA probe. XPS spectra were collected using a monochromatic Al Kα X-ray source (1486.6 eV) to determine the overall composition, and all XPS signals were calibrated using a peak at 284.6 eV (i.e., C 1s core level). Transmission electron microscopy (TEM) results were collected with a Philips Tecnai G2 (FEI-TEM) microscope operating at 200 kV. Fourier transform infrared (FTIR) was measured with the NICOLET 6700 (Thermo Fisher Scientific, USA) equipment. SEM top view images were recorded by the NOVA NANO SEM 450. For the *J-V* test, PSCs were measured at an incident light intensity of 100 mW cm^{-2} (Oriel 71964), which was generated by the 300 W solar simulator (Oriel Sol3A Class AAA Solar Simulator 9043A, Newport) and passed through the AM 1.5 filter (Oriel 74110). We also calibrated the light intensity using the Oriel reference solar cell (Oriel 91150) and corrected it to 1 sun. PL decay profiles were obtained using a fluorescence spectrophotometer (F-4600, Hitachi, Tokyo, Japan) with a 150 W Xe lamp at 466 nm wavelength as the excitation source. In addition, for more information about Grazing-Incidence X-ray Scattering (GIXS) instrumentation, please refer to our previous article.[2]

Supplementary References

1. Huang, S.-K. et al. Unravelling the origin of the photocarrier dynamics of fullerene-derivative passivation of SnO_2 electron transporters in perovskite solar cells. *J. Mater. Chem. A* **8**, 23607-23616 (2020).

2. Lin, C.-Y. et al. Unveiling the nanoparticle-seeded catalytic nucleation kinetics of perovskite solar cells by time-resolved GIXS. *Adv. Funct. Mater.* **29**, 1902582 (2019).