Supporting Information

Thermally stable inverted perovskite solar cells using electropolymerized Zn-porphyrin film as dopant-free hole-transporting layer

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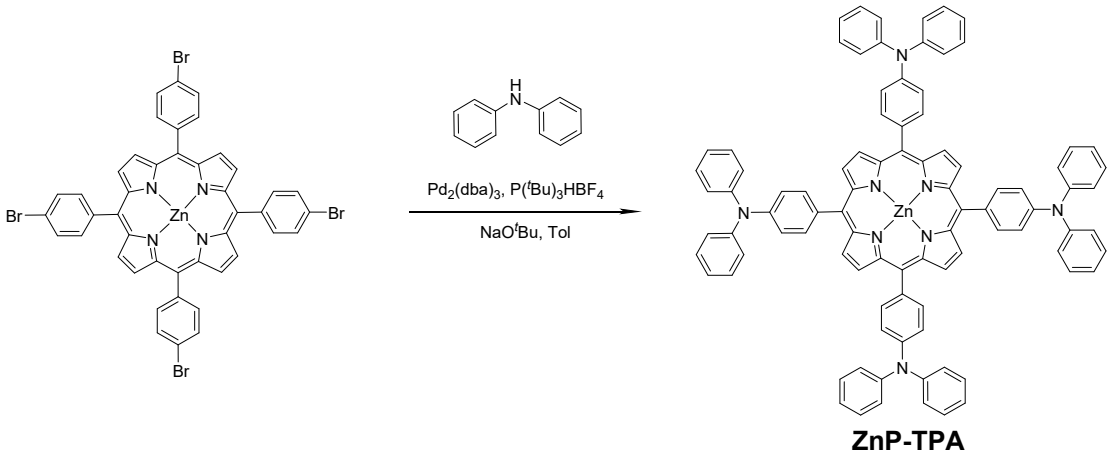

Fig. S1. Schematic diagram of the synthesis route of ZnP-TPA

Synthesis of ZnP-TPA

5,10,15,20-tetra(p-bromophenyl)porphyrin zinc (250.0 mg, 0.25 mmol), diarylamines (212.8 mg, 1.25 mmol), $Pd_2(dba)_3$ (23.0 mg, 0.025 mmol), tri-tert-butylphosphine (0.53 ml, 1M) and sodium tert-butoxide (120.8 mg, 1.25 mmol) were dissolved in toluene (20 mL) and stirred at 120 °C with reflux for 36 h under a nitrogen atmosphere. Followed by the addition of proper amount of water, the resulting solution was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by silica gel chromatography (eluent: petroleum ether/ dichloromathane, 1/1) to yield 257.3 mg of ZnP-TPA in 75.6% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.10 (s, 8H), 8.06 (d, J = 9 Hz, 8H), 7.47-7.37 (m, 40H), 7.13 (m, 8H). MALDI-TOF (m/z): calcd for $C_{92}H_{64}N_8Zn$ 1346.96, found 1347.73.

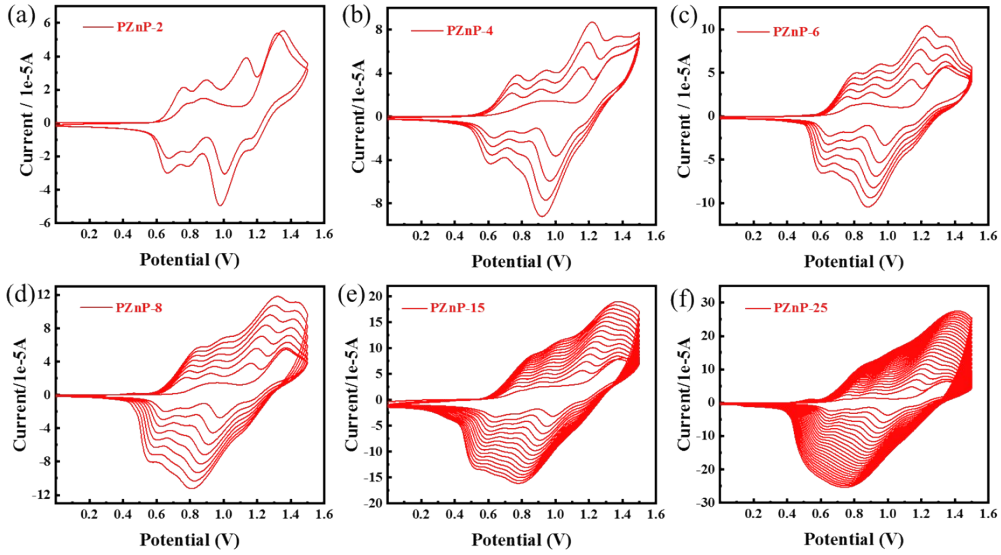

Fig. S2. Cyclic voltammograms recorded during the oxidative electropolymerization of ZnP-TPA (0.12 mg/mL in CH_2Cl_2) on an indium–tin-oxide (ITO) glass electrode with different scan cycles between 0 and +1.5 V at 100 mV/s.

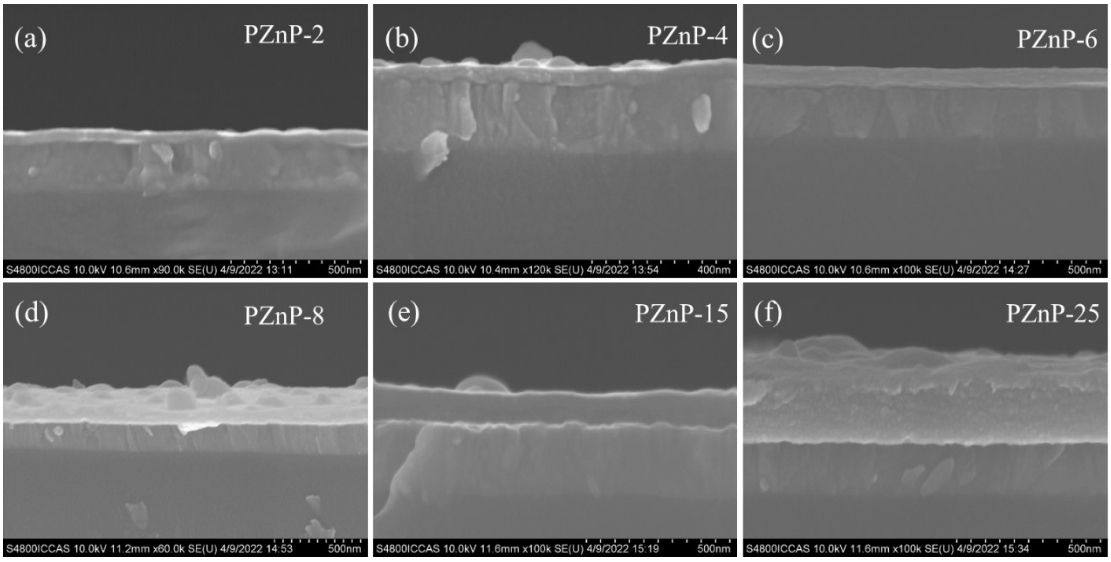

Fig. S3. Cross-section SEM picture of ITO/PZnP film obtained after 2, 4, 6, 8, 15 and 25 scan cycles.

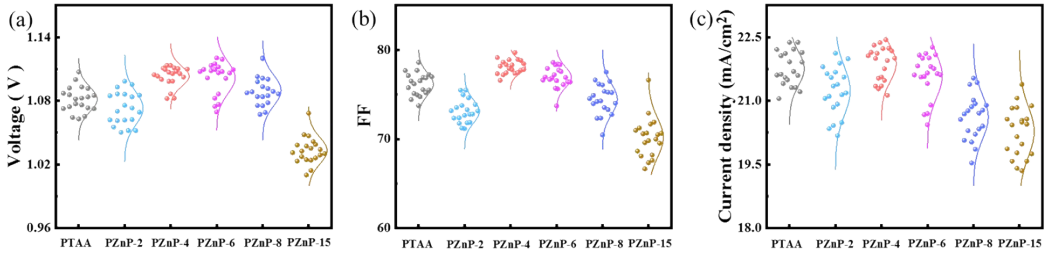

Fig. S4. Statistical diagrams of PSCs performance based on electropolymerized PZnP and PTAA，including V_{oc}, FF, and J_{sc} (20 devices).

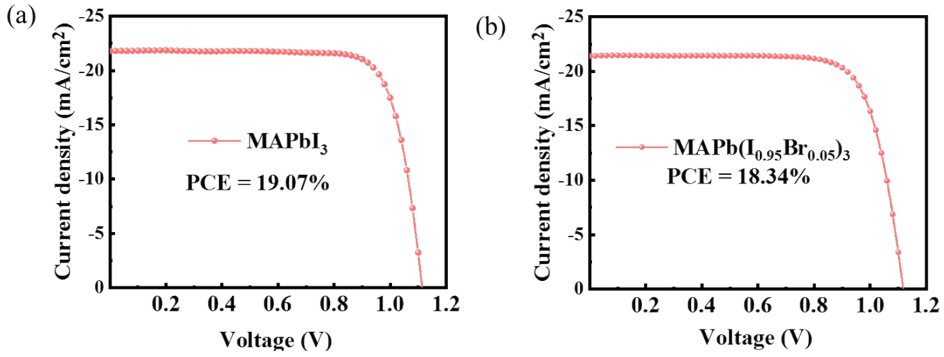

Fig. S5. *J-V* curves of the best-performance of MAPbI3 and $MAPb(I_{0.95}Br_{0.05})_3$ perovskite solar cells.

Table S1 Summary of PZnP-based device parameters with different perovskite materials

Perovskite	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF* (%)	PCE (%)
$MAPbI_3$	21.79	1.11	78.53	19.07
$MAPb(I_{0.95}Br_{0.05})_3$	21.40	1.12	76.68	18.34

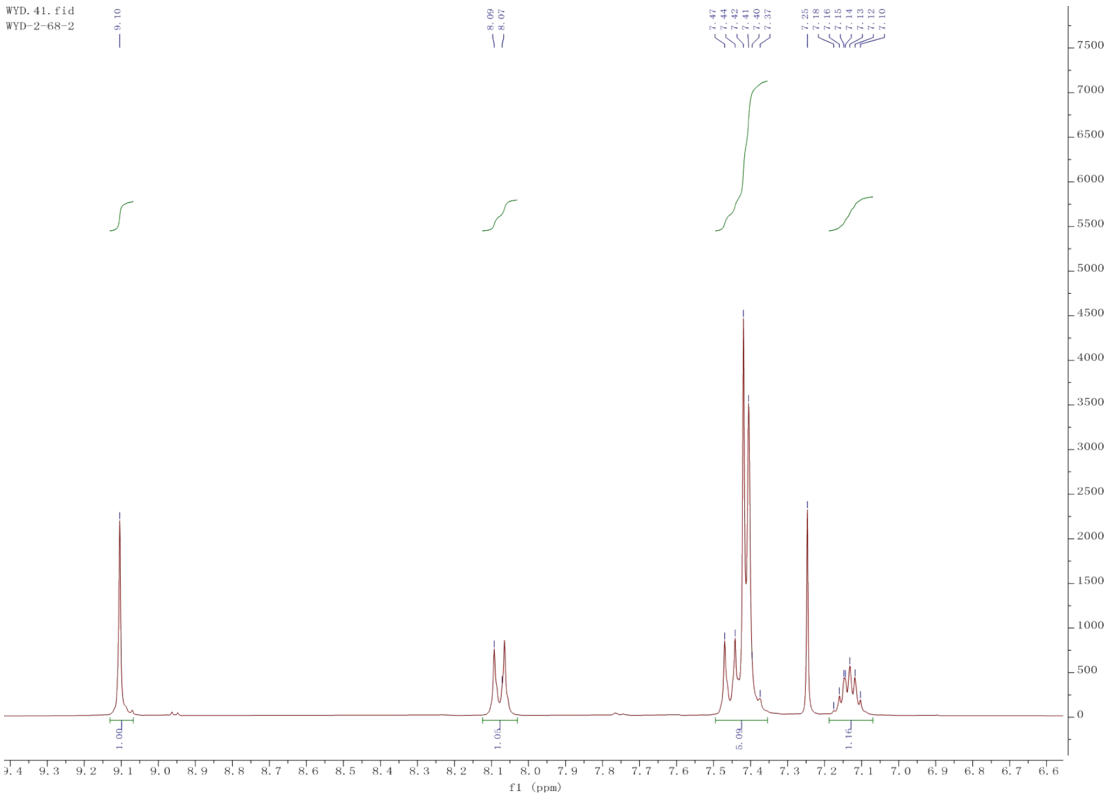

Fig. S6 ^{1}H NMR spectrum of ZnP-TPA in $CDCl_3$.