

Supporting Information

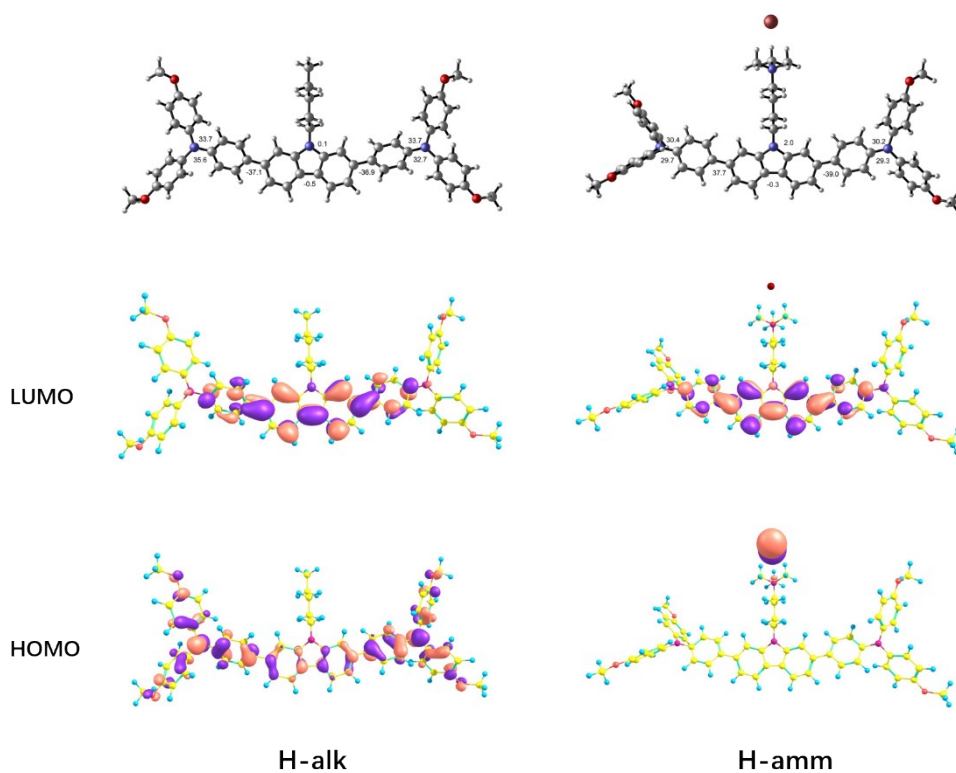


Fig. S1 Optimized geometrical structures, electronic density distributions of HOMO and LUMO of **H-alk** and **H-amm**.

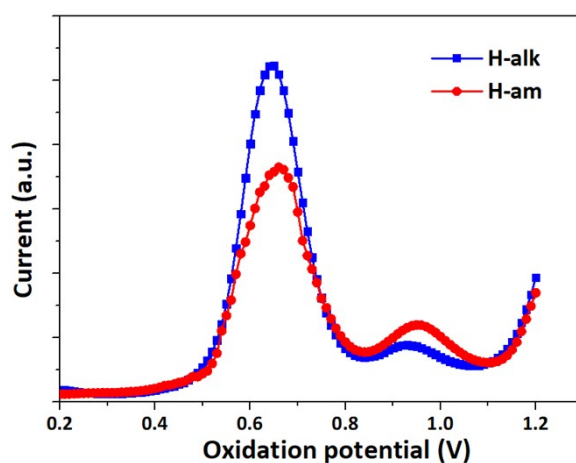


Fig. S2 Differential pulse voltammetry curves of **H-alk** and **H-amm**.

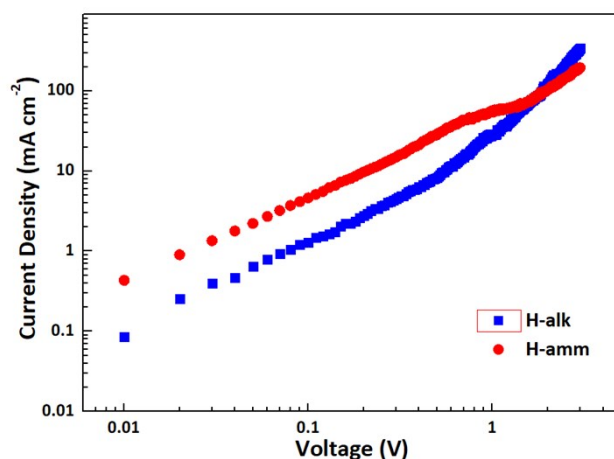


Fig. S3 J - V curves obtained from the hole-only ITO/PEDOT:PSS/HTM/Au device.

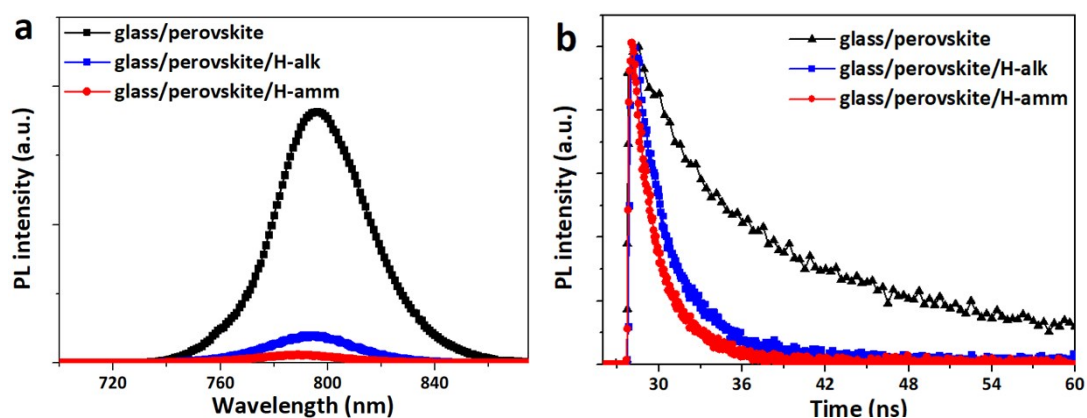


Fig. S4 Photoluminescence spectrum of perovskite film and perovskite/HTM bilayer, and (b) corresponding time-resolved photoluminescence.

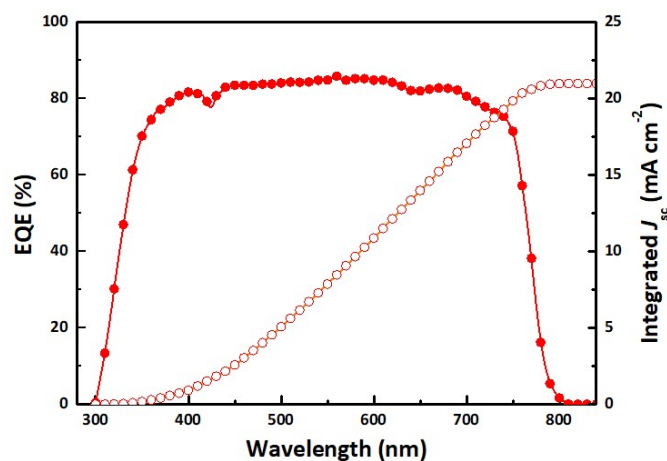


Fig. S5 incident photo-to-current conversion efficiency (IPCE) spectra of the best-performing device with **H-amm** as HTM.

Table S1 Mean values with the standard deviation of photovoltaic parameters of the PSCs with different HTMs. Each group contains 10 independent samples

HTM	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
H-alk	1.07 ± 0.01	21.46 ± 0.26	75 ± 0.97	17.02 ± 0.44

H-amm	1.07±0.01	21.48±0.46	76±1.57	17.44±0.75
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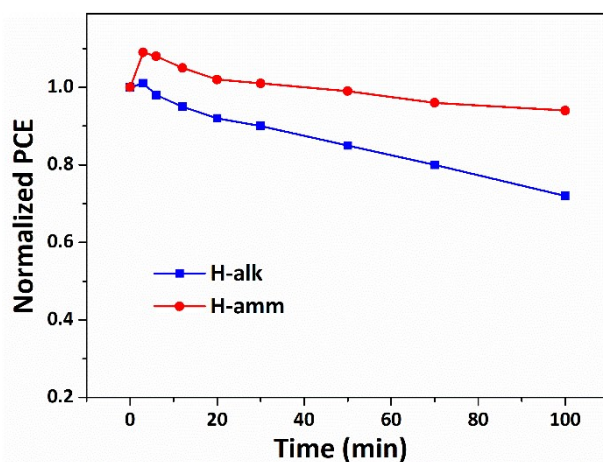


Fig. S6 stability test with illumination.

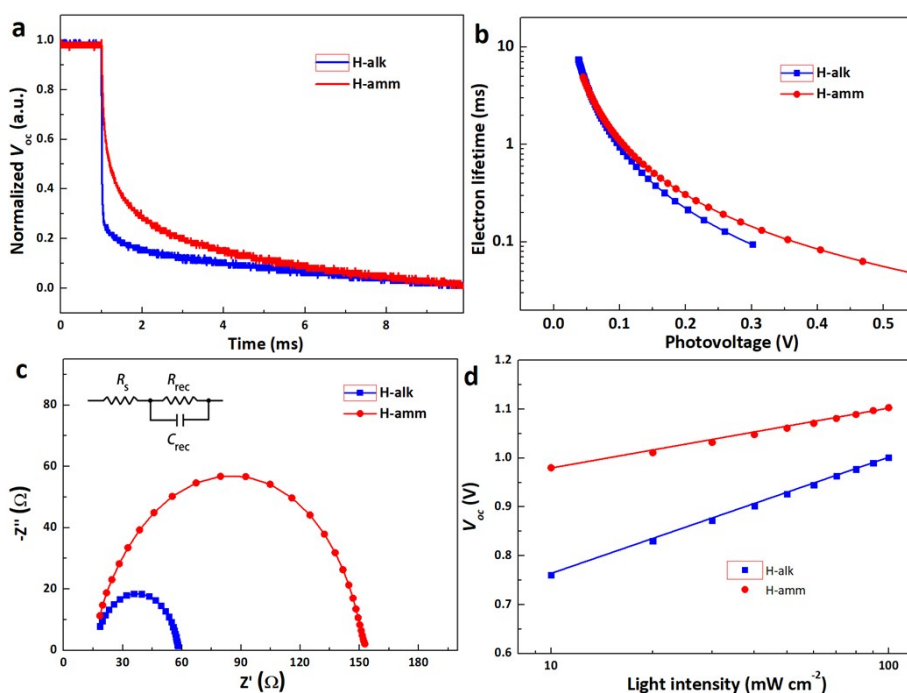
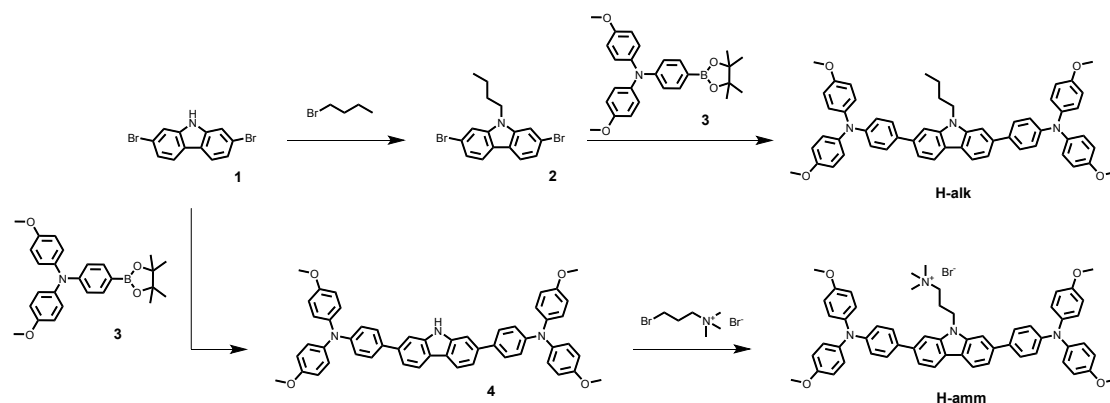


Fig. S7 Electrochemical analysis of devices with different HTMs. (a) Transient photovoltage decay curves. (b) Extracted lifetime of the injected carriers versus photovoltage. (c) Nyquist plots with the equivalent circuit. (d) V_{oc} dependence upon light intensity.

Synthesis

All reagents and chemicals are purchased from Sigma-Aldrich, TCI, Alfa or Sinopharm Chemical Reagent Co., et al. All chemicals are used as received without further processing unless otherwise noted. Compound **3** and compound **4** are prepared in our lab referring to previous literature.



Scheme S1. Synthetic routes for **H-alk** and **H-amm**.

Compound 2

2,7-dibromo-9H-carbazole (1 mmol, 0.325 g), K_2CO_3 (5 mmol, 0.7 g), 15 mL DMF were added into a 50 mL flask and stirred at room temperature for 30 min under Ar. Then heating the mixture system to 80 °C, 1-Bromobutane (1.85 mmol, 0.2 mL) was added to the system. The reaction solution was kept with stirring for 4 h. After cooling to R.T., the reaction mixture was poured into cold Na_2SO_4 aqueous solution, then the crude product precipitates out as solid. The crude product was recrystallized from methanol to obtain compound **2** as white solid (0.30 g, 80%). 1H NMR (500 MHz, DMSO) δ 8.12 (d, $J = 8.3$ Hz, 2H), 7.90 (d, $J = 1.5$ Hz, 2H), 7.36 (dd, $J = 8.3$, 1.6 Hz, 2H), 4.39 (t, $J = 7.2$ Hz, 2H), 1.77 – 1.55 (m, 2H), 1.42 – 1.18 (m, 2H), 0.88 (t, $J = 7.4$ Hz, 3H).

H-alk

Compound 2 (0.19 g, 0.5 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N-bis(4-methoxyphenyl)aniline (compound **3**, 1.2 mmol, 0.52 g), 2M solution of K_2CO_3 (8 mmol, 1.1 g) in H_2O , $[Pd(PPh_3)_4]$ (0.05 mmol, 60 mg), DMF (20 mL) were added into a 50 mL Ar-protected flask. The reaction solution was kept with stirring at 90 °C for 12 h. After cooling to R.T., the reaction mixture was poured into cold Na_2SO_4 aqueous solution, then the crude product precipitates out as solid. The crude product was purified by column chromatography ($CH_2Cl_2/PE = 2:1$) to obtain **H-alk** as light green solid (0.32 g, 78%). 1H NMR (500 MHz, DMSO) δ 8.12 (d, $J = 8.1$ Hz, 2H), 7.75 (s, 2H), 7.65 (d, $J = 8.7$ Hz, 4H), 7.42 (d, $J = 9.1$ Hz, 2H), 7.06 (d, $J = 8.9$ Hz, 8H), 6.92 (dd, $J = 18.1$, 8.8 Hz, 12H), 4.48 (t, $J = 6.7$ Hz, 2H), 3.76 (s, 12H), 1.78 (s, 2H), 1.35 (d, $J = 7.7$ Hz, 2H), 0.89 (t, $J = 7.4$ Hz, 3H).

H-amm

Compound 4 (0.23 g, 0.3 mmol), K_2CO_3 (5 mmol, 0.7 g), 15 mL DMF were added into a 50 mL flask and stirred at room temperature for 30 min under Ar. Then heating the mixture system to 80 °C, (3-bromopropyl)trimethylammonium bromide (0.5 mmol, 0.13 g) was added to the system. The reaction solution was kept with stirring for 4 h. After cooling to R.T., the reaction mixture was poured into cold Na_2SO_4 aqueous solution. Then add HBr to the mixture, the crude product precipitates out as solid. The crude product was washed by methanol and petroleum ether to obtain **H-amm** as light green solid. (0.27 g, 95%). 1H NMR (500 MHz, DMSO) δ 8.16 (d, $J = 8.1$ Hz, 2H), 7.81 (s, 2H), 7.67 (d, $J = 8.7$ Hz, 4H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.07 (d, $J = 8.9$ Hz, 8H), 6.93 (dd, $J = 19.3$, 8.8 Hz, 12H), 4.56 (t, $J = 6.2$ Hz, 2H), 3.76 (s, 12H),

3.04 (s, 9H), 1.25 (m, 2H), 0.87 (m, 2H).

Device Fabrication

The glass/ITO substrate was sequentially washed with isopropanol, acetone, distilled water and isopropanol. The sheet resistance of ITO is $\sim 15 \Omega/\square$ and the thicknesses of glass and ITO are 0.5 mm and 140 nm, respectively. For SnO₂ nanoparticles films, the diluted SnO₂ nanoparticles solution (2.67%) was spin coated on glass/ITO substrates in ambient air, and then annealed at 150 °C for 30 min. After depositing the electron transport layer, the perovskite layer was deposited by a two-step spin coating method; first, 1.3M of PbI₂ in dimethylformamide (DMF) was spin coated onto the electron transport layer at 1,500 r.p.m. for 30 s, then annealed at 70 °C for 30 min; second, after the PbI₂ had cooled down, the mixture solution of FAI:MABr:MACl (60mg:6mg:6mg in 1ml isopropanol) was spin coated onto the PbI₂ at 1,500 r.p.m. for 30 s, and then the film was taken out from the glove box and annealed in ambient air (30%~40% humidity). The annealing was under either 135 °C or 150 °C for 20 min; 150 °C annealing can deliver a higher performance due to the formation of the PbI₂ phase in the perovskite layer. The HTM was subsequently deposited on the substrate by spin-coating at 5000 rpm for 30 s after above substrate cooling to R.T.. The HTM solution were prepared in anhydrous chlorobenzene. the concentration of HTMs is 20 mg mL⁻¹ with 8 μ L of 4-tert-butylpyridine and 15 μ L of lithium bis(trifluoromethylsulphonyl)imide (520 mg mL⁻¹ in acetonitrile). The HTM was deposited on the on ITO/SnO₂/perovskite substrate by spin-coating at 3000 rpm for 30 s. Finally, a ~ 70 nm thick Au counter electrode was deposited on top of above film by thermal evaporation. The active area of the device was defined by a black mask with a size of 0.09 cm² for all measurement.

Characterization

¹H NMR spectra were recorded on a Brücker spectrometer (400 MHz) with chemical shifts against tetramethylsilane (TMS). UV-vis spectra of investigated molecules are carried out on a UV-vis spectrophotometer (SOLID3700, Shimadzu Co. Ltd, Japan). The PL measurements of HTM and perovskite/HTM films were measured on a fluorescence detector (Hitachi F-4600, Japan). Cyclic voltammetry was tested with a CHI660d electrochemical analyzer (CH Instruments, Inc., China). A normal three electrode system was used consisting of a platinum wire counter electrode, a platinum working electrode, as well as a calomel reference electrode. Redox potential of investigated compounds was tested in DCM with 0.1 M tetrabutylammonium hexafluorophosphate with a scan rate of 50 mV s⁻¹. The incident photon-to-current conversion efficiency (IPCE) was recorded on QE/IPCE measurement kit (Newport, USA). The moisture resistance of HTMs was measured on a contact angle tester (METATEST E3-300).