Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Influence of hole transport material ionization energy on performance of perovskite solar cells.

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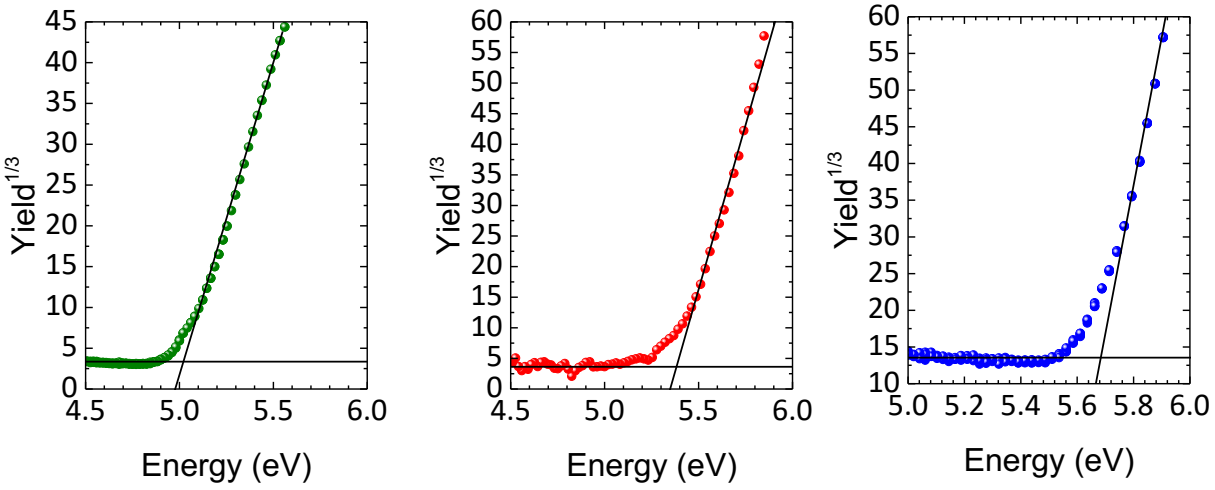

Figure S1. Photo-electron spectroscopy in air (PESA) for m-MTDATA (green), TaTm (red) and TcTa (blue). Solid lines show fitted base and trend lines. From the measurements extracted ionization energys are 5.02eV, 5.38eV, 5.68eV for m-MTDATA, TaTm and TcTa respectively.

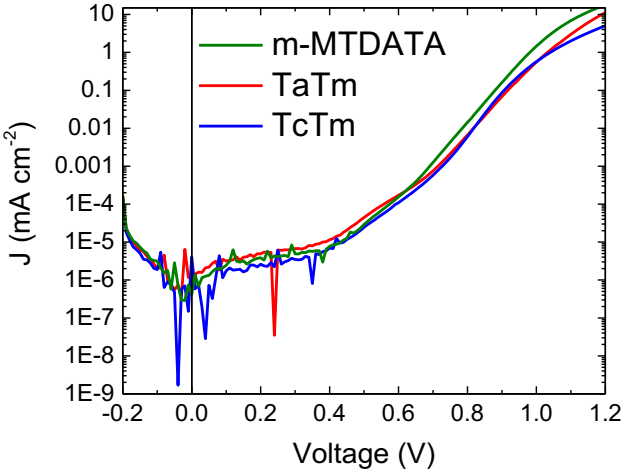

Figure S2. J-V curves in darkness for perovskite solar cells with 5nm thick HTM`s.

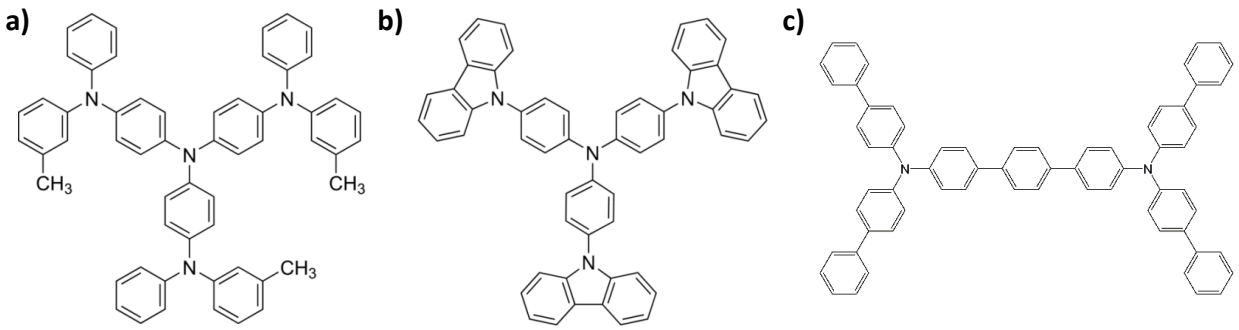

Figure S3. Organic hole-transport materials. a) 4,4',4''-Tris[(3-methylphenyl)phenylamino]triphenylamine (m-MTDATA) , b) Tris(4-carbazoyl-9-ylphenyl)amine (TcTa), c) N4,N4,N400,N400-tetra([1,10-biphenyl]-4-yl)-[1,10:40,100-terphenyl]-4,400- diamine (TaTm).

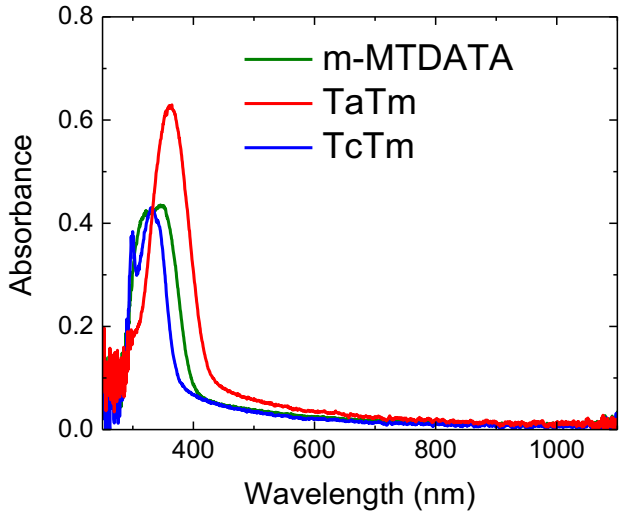

Figure S4. Absorption of organic hole-transport materials

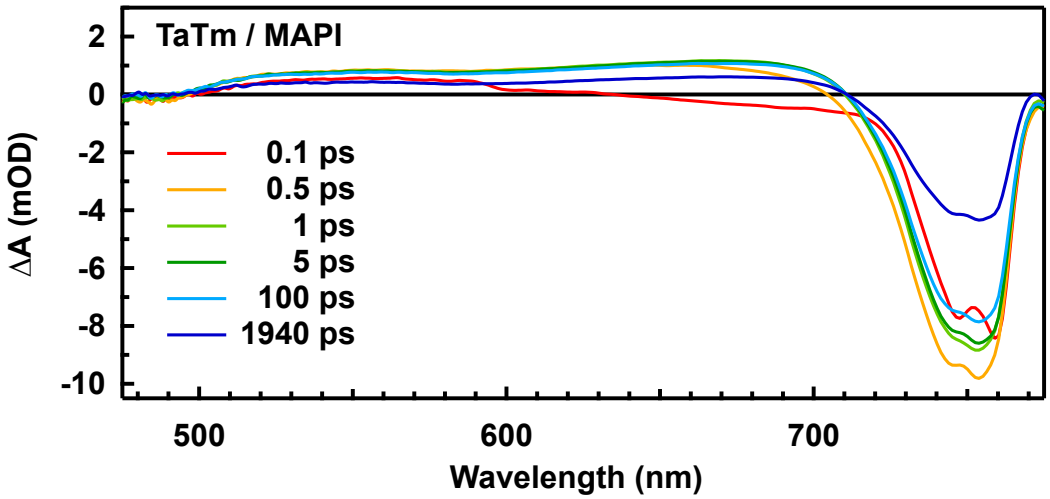

Figure S 5. TA spectra at different time delays for the MAPI/TaTm bilayer excited at 600 nm.

Experimental Section

Perovskite films deposition and diodes fabrication.

ITO-coated glass substrates were subsequently cleaned with soap, water and isopropanol in an ultrasonic bath, followed by UVozone treatment. Substrate were transferred to a vacuum chamber integrated into a nitrogenfilled glovebox (H_2O and O_2 < 0.1 ppm) and evacuated to a pressure of 10^{-6} mbar. The vacuum chamber is equipped with six temperature controlled evaporation sources (Creaphys) fitted with ceramic crucibles. Three quartz crystal microbalance (QCM) sensors are used, two monitoring the deposition rate of each evaporation source and a third one close to the substrate holder monitoring the total deposition rate. For the HTMs we used 4,4',4''-Tris[(3-methylphenyl)phenylamino]triphenylamine (m-MTDATA), Tris(4-carbazoyl-9-ylphenyl)amine (TcTa), N4,N4,N400,N400-tetra([1,10-biphenyl]-4-yl)-[1,10:40,100-terphenyl]-4,400- diamine (TaTm) whereas the fullerene (C_{60}) and 2,9-Dimethyl-4,7- diphenyl-1,10-phenanthroline (BCP) where used as ETM. For thickness calibration we individually sublimed the materials and a calibration factor was obtained by comparing the thickness inferred from the QCM sensors with that measured with a mechanical profilometer (Ambios XP1). After HTL deposition, the chamber was vented with dry N2 to replace the crucibles with those containing the starting materials for the perovskite deposition, PbI_2 and CH_3NH_3I. The vacuum chamber was

evacuated again to a pressure of 10^{-6} mbar, and the perovskite films were then obtained by co-deposition of the two precursors. MAI was evaporated with a temperature of approximately 70 ºC and PbI_2 with a temperature between 255 ºC and 300 ºC to obtain a final perovskite thickness of around 600 nm. After deposition of the perovskite films, the chamber was vented and the crucibles replaced with those containing C60 and BCP, and evacuated again to a pressure of 10-6 mbar. Finally the substrates were transferred to a second vacuum chamber where the silver top contact (100 nm thick) was deposited.

Device characterization.

The external quantum efficiency (EQE) was estimated using the cell response at different wavelength (measured with a white light halogen lamp in combination with band-pass filters), where the solar spectrum mismatch is corrected using a calibrated Silicon reference cell (MiniSun simulator by ECN, the Netherlands). The current density-voltage (J-V) characteristics were obtained using a Keithley 2612A source measure under white light illumination using a solar simulator by Abet Technologies (model 10500 with an AM1.5G xenon lamp as the light source). The scan rate was 0.1 V/s. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode equipped with an infrared cut-off filter (KG-3, Schott).

Femtosecond Transient Absorption Spectroscopy:

Experimental set-up:

Transient absorption (TA) measurements were performed with 600 nm pulsed excitation, generated in an optical parametric amplifier (OPerA, Coherent) from the fundamental pulses of an amplified Ti:sapphire laser system (35 fs, 800 nm, 1 kHz, 6 mJ, Astrella, Coherent). The broadband white light probe pulses were generated by focusing the fundamental beam on a sapphire plate, then split into a reference and a signal component. The pump pulses were chopped at half the laser frequency to allow shot-to-shot detection. The pump and probe beam diameters were measured with a beam profilometer (1 mm and 260 µm, respectively), ensuring a uniform distribution of detected photo-excited species. The probe pulses were temporally delayed relative to the excitation pulses via a micrometer translation stage, and pump-probe delays up to 2 ns were measured. The probe pulses transmitted through the sample and the reference probe pulses were spectrally dispersed in a home-build prism spectrograph, assembled by

Entwicklungsbüro Stresing (Berlin) and detected shot-to-shot by a pair of back-thinned silicon CCDs (Hamamatsu S07030-0906).