

Electronic Supplementary Information

Cross-Linkable Carbazole-Based Hole Transporting Materials for Perovskite Solar Cells

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Table of Contents

General methods	S2
Detailed synthetic procedures	S2–S6
Thermal Properties	S7
Ionization Potential Measurements	S7
Hole Drift Mobility Measurements	S7-S10
Fabrication of the devices	S11
UV/vis spectra of the not heated and cross-linked HTM films, before and after washing with DMF:DMSO	S11-S12
Stability of the devices	S12
References	S13

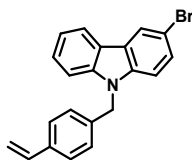
Materials and HTMs synthesis

Chemicals were purchased from Sigma-Aldrich, TCI Europe and used as received without further purification. ^1H NMR spectra were recorded at 400 MHz on a Bruker Avance III spectrometer with a 5 mm double resonance broad band BBO z-gradient room temperature probe, ^{13}C NMR spectra were collected using the same instrument at 101 MHz. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). All the NMR experiments were performed at 25 °C. Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyser, Model 440 C/H/N/.

Thermogravimetric analysis (TGA) was performed on a Q50 thermogravimetric analyzer (TA Instruments) at a scan rate of 10 °C min⁻¹ under nitrogen atmosphere. The values are given for a weight-loss of 5% (T_{d5}). Differential scanning calorimetry (DSC) was performed on a TA Instruments Q2000 differential scanning calorimeter under nitrogen atmosphere. Heating and cooling rate is 10 °C min⁻¹.

UV–vis spectral analysis of the sample in solution (THF, 10⁻⁴ mol l⁻¹) was performed on a Perkin Elmer Lambda 35 UV/VIS spectrophotometer. Diffraction grating crack width is 2 nm. Spectral recording speed is 2 nm s⁻¹. The layer thickness of the solution is $d = 1$ cm. The wavelength λ is given in nm. The time-resolved fluorescence spectra of the sample in solution (THF, 10⁻⁴ mol l⁻¹) were recorded on an Edinburgh Instruments FLS920 light emission intensity spectrophotometer. The layer thickness of the solution is $d = 1$ cm. The crack width of the diffraction grating is 1.5 nm. The wavelength λ is given in nm.

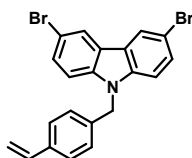
3-bromo-9-(4-vinylbenzyl)-9H-carbazole (1)



3-bromocarbazole (1 g, 4.1 mmol, 1 eq) was dissolved in dimethylsulfoxide (25 mL) and purged with argon for 30 minutes. Afterwards, benzyltriethylammonium chloride (0.1 eq) and 50% NaOH (0.4 mL) solution were added. When the reaction mixture turned red 4-vinylbenzylchloride (0.63 mL, 4.5

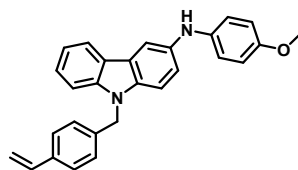
mmol, 1.1 eq) was slowly dropped and the mixture was stirred at room temperature for 3 hours under argon atmosphere. The obtained product was filtered off and washed with ethanol to collect **2** as a white solid (1.25 g, 85%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.44 (s, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.69 – 7.59 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.65 (2d, *J*₁ = 17.6, *J*₂ = 10.9 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.66 (s, 2H), 5.20 (d, *J* = 10.9 Hz, 1H). ¹³C NMR (101 MHz, DMSO) 140.98, 139.34, 137.63, 136.75, 136.59, 128.63, 127.47, 127.15, 126.84, 124.68, 123.44, 121.73, 121.41, 119.97, 114.76, 112.08, 111.70, 110.32, 45.93.

3,6-dibromo-9-(4-vinylbenzyl)-9*H*-carbazole (**2**)



3,6-dibromocarbazole (1.5 g, 4.6 mmol, 1 eq) was dissolved in dimethylsulfoxide (40 mL) and purged with argon for 30 minutes. Afterwards, benzyltriethylammonium chloride (0.1 eq) and 50% NaOH (0.5 mL) solution were added. When the reaction mixture turned dark yellow 4-vinylbenzylchloride (0.72 mL, 5.1 mmol, 1.1 eq) was slowly dropped and the mixture was stirred at room temperature for 12 hours under argon atmosphere. After that, was extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄, filtered and solvent evaporated. The obtained product was white crystals. The product washed three times with ethanol and filtered off to collect **2** as white crystals (1.84 g, 90%). Spectral data is in agreement with the values reported in the literature [1].

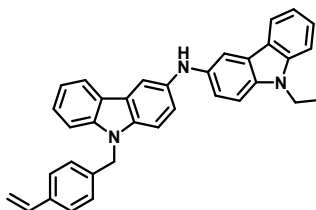
N-(4-methoxyphenyl)-9-(4-vinylbenzyl)-9*H*-carbazol-3-amine (**3**)



Anhydrous dioxane (10 mL) with few drops of distilled water (0.02 eq) was purged with argon for 20 minutes. After that, the temperature was raised to 80 °C, palladium (II) acetate (0.005 eq) and XPhos (0.015 eq) were added. The mixture was stirred for 1.5 minutes and temperature was raised to 110 °C. Compound **1** (2 g, 5.5 mmol, 1 eq), *p*-Anisidine (0.8 g, 6.6 mmol, 1.2 eq) and sodium *tert*-butoxide

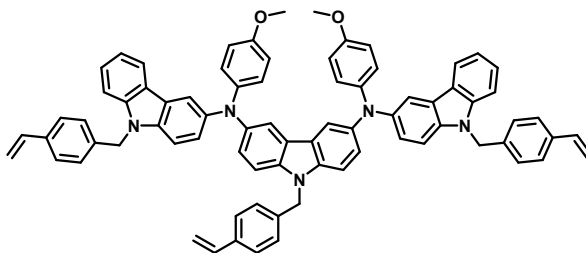
(1.4 eq) were added and stirred for 5 minutes. After cooling to room temperature, reaction mixture was extracted with ethyl acetate and distilled water. The organic layer was dried over anhydrous Na_2SO_4 , filtered and the solvent evaporated. The crude product was purified by column chromatography using 1:9 v/v THF/*n*-hexane as an eluent. Pale gray solid were collected as a final product (1.74 g, 78%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.02 (d, $J = 7.6$ Hz, 1H), 7.75 (s, 1H), 7.65 (s, 1H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 1H), 7.38 – 7.28 (m, 3H), 7.16 – 7.06 (m, 4H), 6.99 (d, $J = 8.6$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 6.62 (2d, $J_1 = 17.6$, $J_2 = 10.9$ Hz, 1H), 5.70 (d, $J = 17.6$ Hz, 1H), 5.54 (s, 2H), 5.16 (d, $J = 10.9$ Hz, 1H), 3.67 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.16, 141.02, 139.32, 138.20, 137.83, 136.66, 136.63, 135.67, 127.51, 126.79, 126.09, 123.28, 122.50, 120.78, 118.92, 118.87, 118.12, 115.10, 114.64, 110.58, 109.87, 108.63, 55.72, 45.87.

9-ethyl-*N*-[9-(4-vinylbenzyl)-9*H*-carbazol-3-yl]-9*H*-carbazol-3-amine (4)



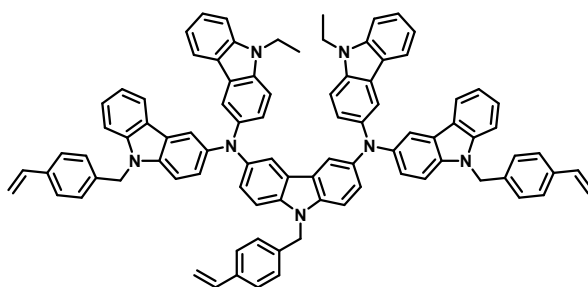
Anhydrous dioxane (10 mL) with few drops of distilled water (0.02 eq) was purged with argon for 20 minutes. After that, the temperature was raised to 80 °C, palladium (II) acetate (0.005 eq) and XPhos (0.015 eq) were added. The mixture was stirred for 1.5 minutes and temperature was raised to 110 °C. Compound **1** (2 g, 5.5 mmol, 1 eq), 3-amino-9-ethylcarbazole (1.4 g, 6.6 mmol, 1.2 eq) and sodium *tert*-butoxide (1.4 eq) were added and stirred for 10 minutes. After cooling to room temperature, reaction mixture was extracted with ethyl acetate and distilled water. The organic layer was dried over anhydrous Na_2SO_4 , filtered and the solvent evaporated. The crude product was purified by column chromatography using 1:9 v/v THF/*n*-hexane as an eluent. Pale green solid were collected as a final product (1.82 g, 67%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.11 – 7.90 (m, 2H), 7.85 – 7.74 (m, 3H), 7.56 – 7.44 (m, 4H), 7.41 – 7.30 (m, 4H), 7.29 – 7.18 (m, 2H), 7.17 – 7.03 (m, 4H), 6.62 (2d, $J_1 = 17.6$, $J_2 = 10.9$ Hz, 1H), 5.71 (d, $J = 17.6$ Hz, 1H), 5.56 (s, 2H), 5.17 (d, $J = 10.9$ Hz, 1H), 4.46 – 4.27 (m, 2H), 1.37 – 1.19 (m, 3H). ^{13}C NMR (101 MHz, DMSO) δ 141.02, 140.38, 138.99, 138.25, 138.17, 136.67, 136.63, 135.51, 135.14, 127.53, 126.79, 126.03, 125.89, 123.37, 123.26, 122.55, 122.45, 120.80, 118.87, 118.80, 118.50, 118.34, 114.64, 110.63, 110.14, 109.85, 109.65, 109.36, 108.79, 107.89, 45.89, 37.39, 14.24.

***N*³,*N*⁶-bis(4-methoxyphenyl)-9-(4-vinylbenzyl)-*N*³,*N*⁶-bis[9-(4-vinylbenzyl)-9*H*-carbazol-3-yl]-9*H*-carbazole-3,6-diamine (V1205)**



A solution of compound **2** (0.5 g, 1.1 mmol, 1 eq) and compound **3** (1.4 g, 3.4 mmol, 3 eq) in anhydrous toluene (12 mL) was purged with argon for 30 minutes. Afterwards, palladium (II) acetate (0.02 eq), tri-*tert*-butylphosphonium tetrafluoroborate (0.027 eq) and sodium *tert*-butoxide (3 eq) were added and the solution was refluxed under argon atmosphere for 8 hours. After cooling to room temperature, reaction mixture was extracted with ethylacetate and distilled water, filtered through celite. The organic layer was dried over anhydrous Na₂SO₄, filtered and solvent evaporated. The crude product was purified by column chromatography using 3:22 v/v acetone/*n*-hexane as an eluent. The obtained product was precipitated from acetone into 15 times excess of *n*-hexane. The precipitate was filtered off and washed with ethanol to collect **V1205** as a pale green solid (0.89 g, 72%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 4H), 7.59 – 7.43 (m, 6H), 7.40 – 7.30 (m, 8H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.03 (m, 10H), 6.83 (d, *J* = 8.9 Hz, 4H), 6.75 (d, *J* = 8.9 Hz, 4H), 6.70 – 6.57 (m, 3H), 5.81 – 5.66 (m, 3H), 5.54 (s, 6H), 5.26 – 5.11 (m, 3H), 3.65 (s, 6H). ¹³C NMR (101 MHz, DMSO) δ 154.19, 143.43, 141.74, 141.38, 141.09, 138.00, 137.67, 136.80, 136.72, 136.66, 136.61, 127.68, 127.56, 126.85, 126.79, 126.30, 124.91, 124.03, 123.48, 123.34, 123.30, 122.40, 120.95, 119.20, 117.21, 116.08, 115.04, 114.66, 110.96, 110.76, 109.94, 55.60, 45.94. Anal. calcd for C₇₇H₆₁N₅O₂: C, 84.98; H, 5.65; N, 6.43; found: C, 85.17; H, 5.54.; N, 6.41.

***N*³,*N*⁶-bis(9-ethyl-9*H*-carbazol-3-yl)-9-(4-vinylbenzyl)-*N*³,*N*⁶-bis[9-(4-vinylbenzyl)-9*H*-carbazol-3-yl]-9*H*-carbazole-3,6-diamine (V1206)**



A solution of compound **2** (0.5 g, 1.1 mmol, 1 eq) and compound **4** (1.7 g, 3.4 mmol, 3 eq) in anhydrous toluene (13 mL) was purged with argon for 30 minutes. Afterwards, palladium (II) acetate (0.02 eq), tri-*tert*-butylphosphonium tetrafluoroborate (0.027 eq) and sodium *tert*-butoxide (3 eq) were added and the solution was refluxed under argon atmosphere for 23 hours. After cooling to room temperature, reaction mixture was extracted with ethylacetate and distilled water, filtered through celite. The organic layer was dried over anhydrous Na₂SO₄, filtered and solvent evaporated. The crude product was purified by column chromatography using 1.1:3.9 v/v THF/*n*-hexane as an eluent. The obtained product was precipitated from THF into 15 times excess of *n*-hexane. The precipitate was filtered off and washed with ethanol to collect **V1206** as a pale green solid (0.94 g, 66%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.83 – 7.77 (m, 4H), 7.75 – 7.70 (m, 6H), 7.52 – 7.43 (m, 6H), 7.39 – 7.26 (m, 14H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.03 (m, 10H), 7.01 – 6.93 (m, 4H), 6.67 – 6.50 (m, 3H), 5.74 – 5.61 (m, 3H), 5.48 (s, 6H), 5.22 – 5.10 (m, 3H), 4.26 (q, *J* = 7.0 Hz, 4H), 1.19 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (101 MHz, DMSO) δ 142.82, 142.26, 141.05, 140.39, 137.99, 137.45, 136.59, 136.38, 136.00, 127.70, 127.55, 126.82, 126.74, 126.01, 123.73, 123.41, 123.32, 122.42, 122.30, 120.87, 119.05, 118.70, 115.67, 114.88, 114.60, 110.62, 110.24, 109.84, 109.36, 45.91, 37.35, 14.16. Anal. calcd for C₉₁H₇₁N₇: C, 86.57; H, 5.67; N, 7.77; found: C, 86.37; H, 5.64.; N, 7.81.

Thermal Properties

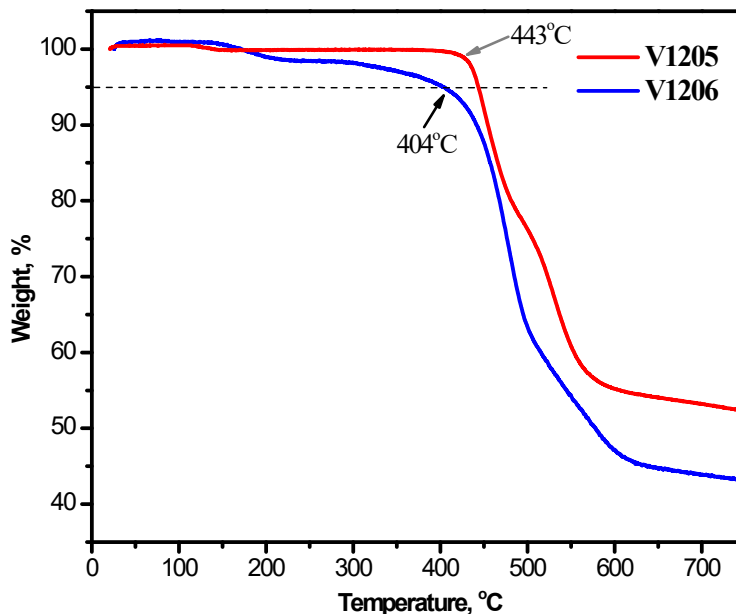


Figure S1. TGA curves of V1205 and V1206. Heating rate 10 °C min⁻¹.

Ionization Potential Measurements

The ionization potential was investigated by the electron photoemission method. The study is performed in an air atmosphere. The sample solutions (THF) were poured onto an aluminium-coated glass plates coated with an adhesive layer of a copolymer of methyl methacrylate and methacrylic acid. The V1205 and V1205 solutions were at a concentration of about 3 mg/ml, and about 100 µl was used for the sample. Two samples were prepared for each material. Heating was performed in a glovebox – V1205 was heated for 90 min at 200°C, V1206 - for 60 min at 300°C. A diffraction grating monochromator with a deuterium lamp was used for the experiment. The power of the falling light was $\sim 5 \cdot 10^{-8}$ W. A negative voltage (-100 V) was connected to the test sample. The electron photoemission current was measured with an open Geiger–Müller counter [2]. The measurement method error was evaluated as 0.03 eV.

Hole Drift Mobility Measurements

Carrier drift mobility was evaluated by the xerographic time-of-flight (XTOF) method. The layers of pure material produced for the hole transport studies with a thickness of 2-3 µm were of poor quality due to cracking and were not suitable for XTOF measurements due to rapid discharging. Therefore, the charge transport was

studied in detail in layers of blends with bisphenol Z-polycarbonate (PC-Z), in weight ratios of 1:1, 1:2 and 1:3. The material solution (THF) was poured onto an aluminum-coated glass plates. The layers were dried at 60°C. The thickness of the transport layer was measured with an optical microscope-interferometer. The drift mobility of holes (μ) was determined in xerographic mode at an electric field of $(0.1 \div 1) \cdot 10^6$ V/cm. Based on the exponential dependence of the charge carrier mobility on the average distance between the charge transporting molecules³, interpolated mobility values were found for the case when the material is pure. For estimation of drift mobility with time-of-flight (TOF) technique sandwich structures were prepared by drop casting 10mg/ml solution of **V1205** and **V1206** in chlorobenzene on FTO. For crosslinking samples of **V1205** and **V1206** were heated at 200°C and 300°C respectively for 90 min and 60 min. Top contact of aluminium was evaporated after samples were prepared. Measurements were performed with constant voltage and short UV laser pulse ($\lambda=355$ nm, 4ns).

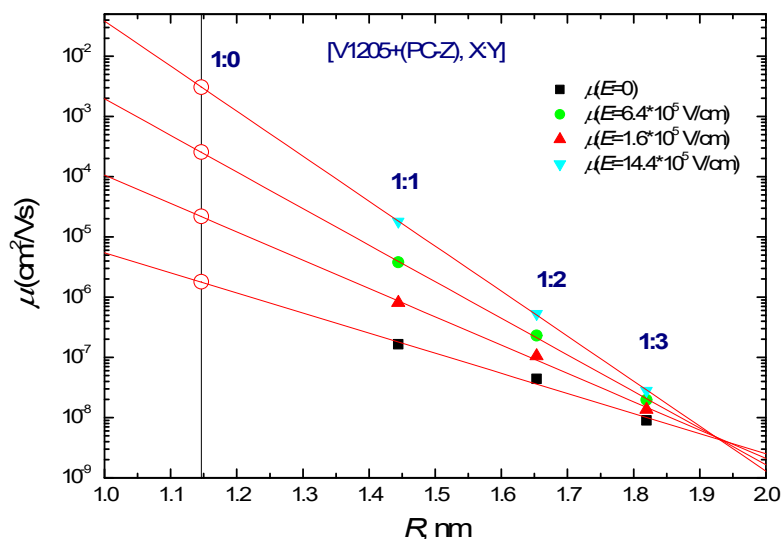


Figure S2. Dependence on the average distance between transporting molecules of **V1205**. When the mean distance between molecules $R = 1,14$ nm is pure substance, we extrapolate the mobility values for that distance

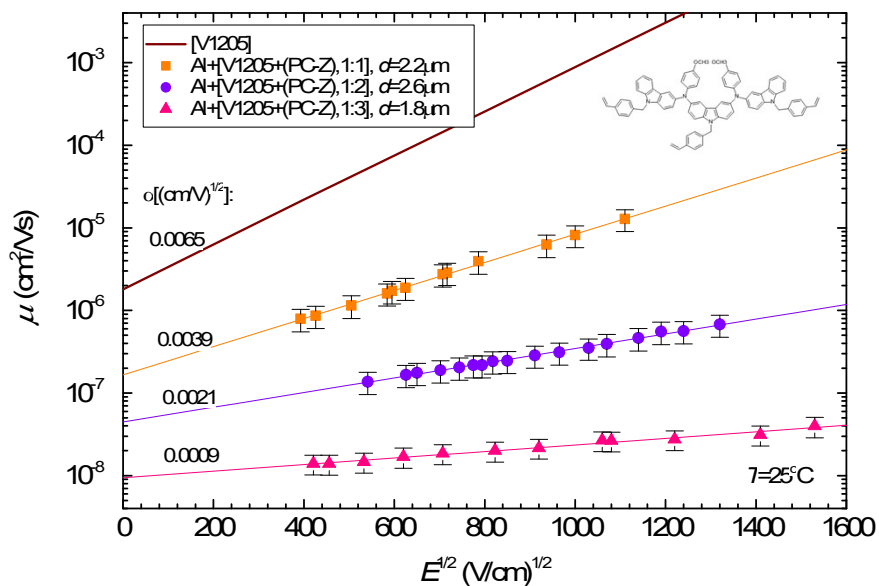


Figure S3. Electric field dependencies of the hole drift mobilities in **V1205** compounds with bisphenol Z-polycarbonate (PC-Z). Extrapolated hole mobility dependencies for pure **V1205** represented as solid line.

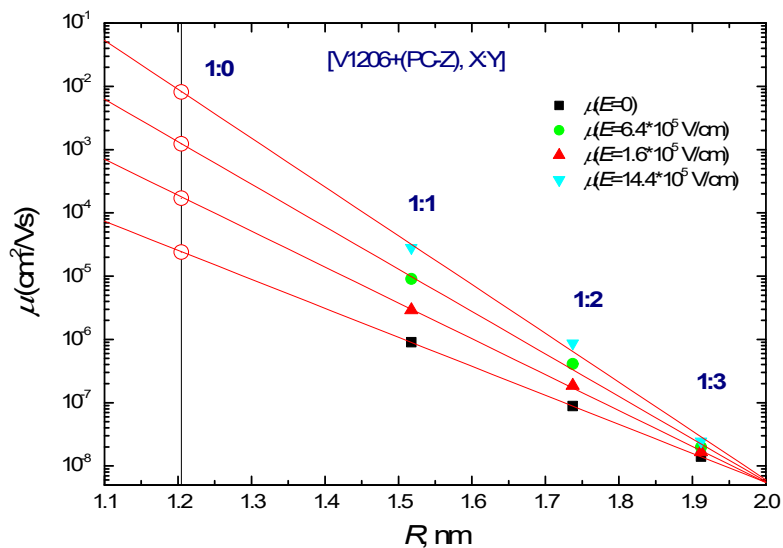


Figure S4. Dependence on the average distance between transporting molecules of **V1206**. When the mean distance between molecules $R = 1,204$ nm is pure substance, we extrapolate the mobility values for that distance

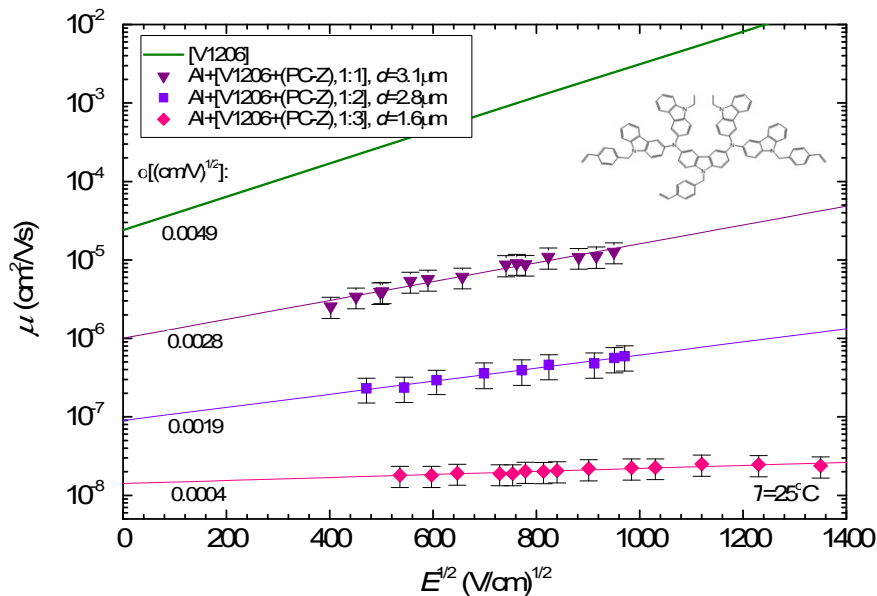


Figure S5. Electric field dependencies of the hole drift mobilities in **V1206** compounds with bisphenol Z-polycarbonate (PC-Z). Extrapolated hole mobility dependences for pure **V1206** represented as solid line.

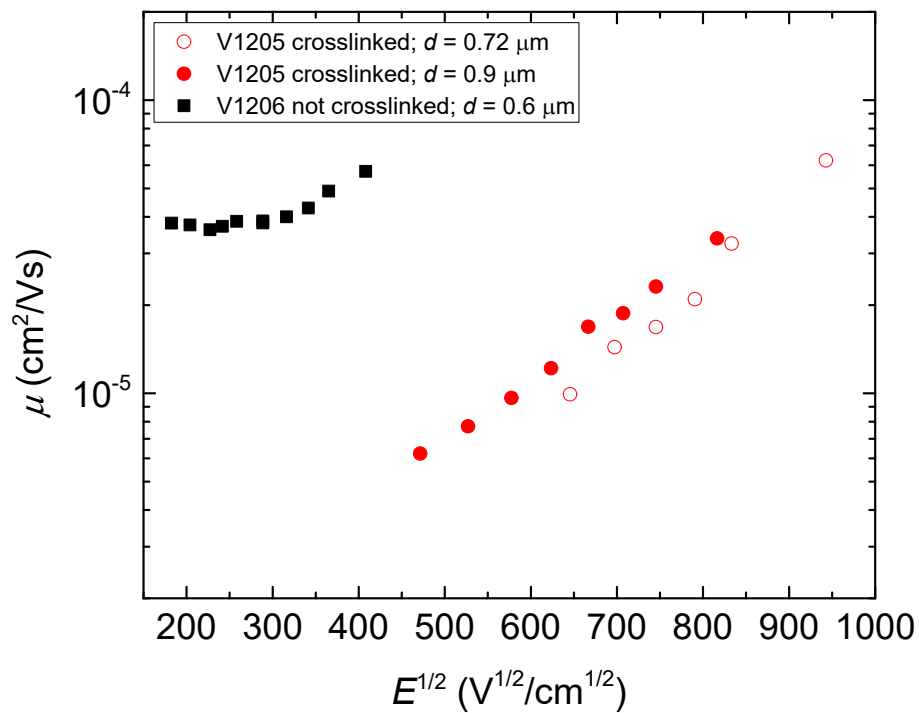


Figure S6. Hole mobility dependence on electric field in crosslinked **V1205** (circles) and not crosslinked **V1206**.

Fabrication of the devices

ITO substrates were pre-cleaned by consequentially sonicating for 15 min in Extran detergent, deionized water, acetone, and 2-propanol. After that, substrates were cleaned by UV-ozone for 15 min. All of the next steps were performed in the N₂-filled glovebox. HTMs were deposited from the 1.5 mg/ml solutions in Toluene by dynamic spin-coating at 6000 rpm (3 s ramp) for 30 s. For the cross-linking, the substrates were annealed at 200°C (1.5h) for **V1205** and at 300°C (1h) for **V1206**. After that, perovskite solution (507 mg PbI₂, 73.4 mg PbBr₂, 172 mg FAI, 22.4 mg MABr dissolved in 0.8 ml DMF and 0.2 ml DMSO, followed by the addition of 40 µl of stock CsI solution (390 mg CsI in 1 ml DMSO)) was statically spin-coated at 5000 rpm (1.7 s ramp) for 35 s, followed by dispensing 300 µl of Anisole after 10 s of spinning program. After spin-coating the substrates were annealed at 100°C for 1h. The device was finalized by evaporation of the LiF (1 nm), C60 (23 nm), BCP (8 nm) and Ag (100 nm).

UV/vis absorption of the not heated and cross-linked films

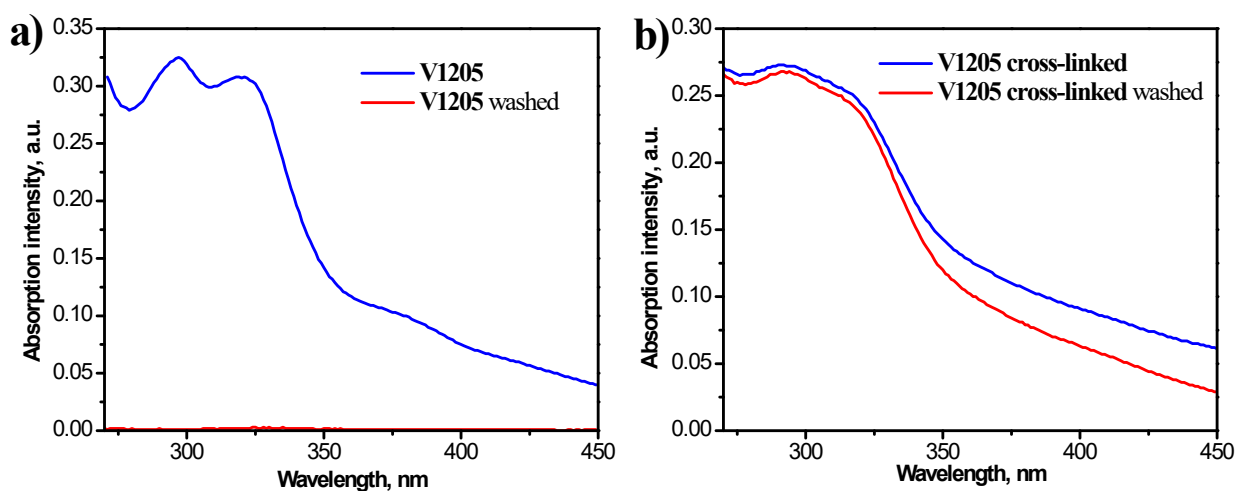


Figure S7. UV/vis spectra of the not heated (a) and cross-linked (b) **V1205** films, before and after washing with DMF:DMSO = 4:1.

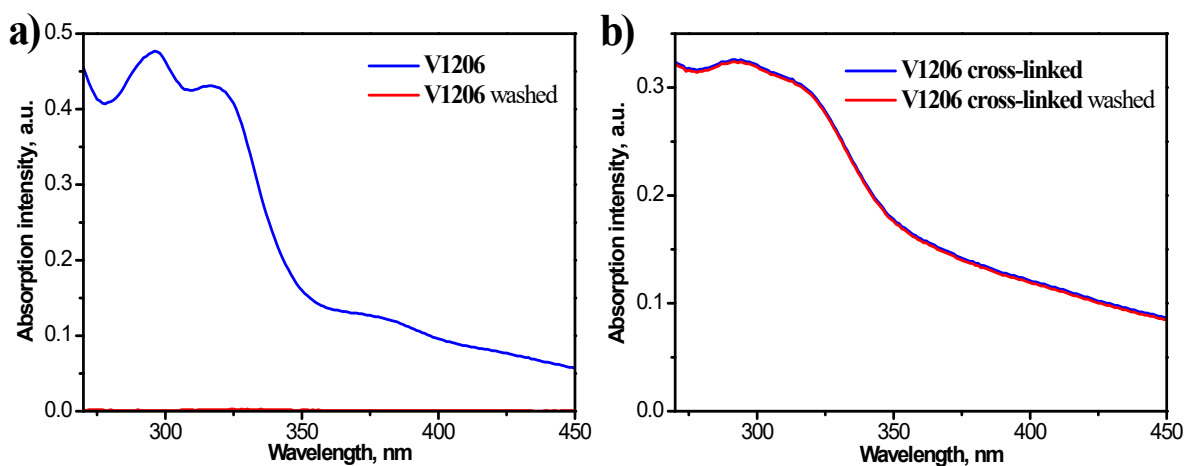


Figure S8. UV/vis spectra of the not heated (a) and cross-linked (b) V1206 films, before and after washing with DMF: DMSO = 4:1.

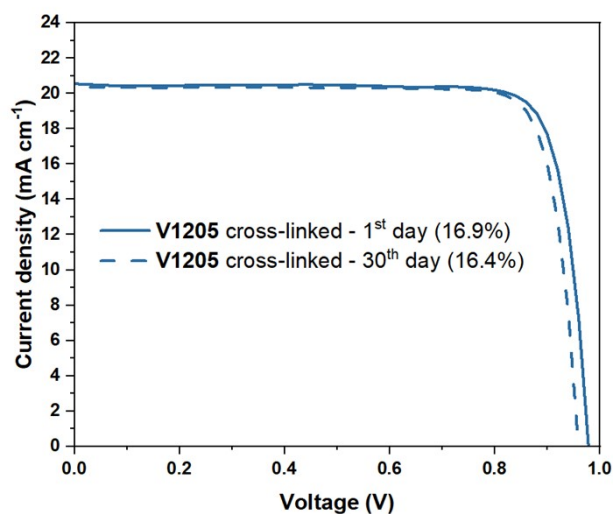


Figure S9. J/V measurements of the fresh and aged device with cross-linked V1205 HTM, reverse scan.

Table S1. Performance parameters of the fresh and aged devices. The data extracted from J/V scans (reverse and forward), and includes averages with standard deviation, as well as best value (in brackets). The relative values are shown in [square brackets].

V1205 cross-linked	J_{SC} , mA cm ⁻¹	V_{OC} , mV	FF , %	PCE , %
1 st day	20.4±0.2 (20.6)	971±6 (979)	82.8±1.1 (84.4)	16.4±0.2 (16.9)
30 th day	19.9±0.3 (20.4) [97.5% (99.0%)]	937±12 (960) [96.5% (98.0%)]	83.6±0.7 (84.5) [101.0% (100.1%)]	15.6±0.4 (16.4) [95.1% (97%)]

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