

Electronic Supplementary Information (ESI)

Cooperating with additives: low-cost hole-transporting materials for improved stability of perovskite solar cells

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General remarks. Reagents and solvents were purchased from standard commercial sources (Aldrich® and Honeywell Riedel-de-Haën™, respectively), while chemical manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. The reaction courses were monitored by thin-layer chromatography (TLC) on Merck® silica gel 60 F254 aluminum sheets. For the cost evaluation of the final HTMs and their intermediates, the prices applied in May 2024 were used. The following restrictions were applied to standardize the calculation for auxiliary material consumption: volumes of each work-up extraction solvent were set to 50 mL and the cost of the drying agent was considered negligible. The total volume of solvents used for flash-chromatography purifications was approximated to 500 mL.

HTM characterization. ^1H NMR spectra were recorded on a Bruker Avance DPX 300 MHz instrument. UV-Vis spectra were recorded in o-dichlorobenzene solutions ($\sim 10^{-5}$ M) on a Jasco V-670 instrument. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 6 TGA instrument under a nitrogen flow (40 mL/min) at a 10 °C/min heating rate. Differential scanning calorimetry (DSC) was recorded on a Q2000 TA instrument under a nitrogen flow (50 mL/min) at a temperature scan of 10 °C/min. The cyclic voltammetry experiments were carried out on a Metrohm Autolab PGSTAT 302-N potentiostat in dichloromethane (HTM concentration: $\sim 10^{-4}$ M) containing tetrabutylammonium tetrafluoroborate (0.10 M) as the supporting electrolyte at a 100 mV/s scan rate. The potentials were measured with respect to Ag/Ag⁺ quasi-reference electrode, that was calibrated against ferrocene (Fc) after each experiment.

Charge transport characterization. The hole mobility of HTM films was measured by employing the space-charge-limited current (SCLC) method. For this purpose, typical hole-only devices were fabricated in a structure of glass/ITO/PEDOT:PSS/HTM/MoO₃/Au. The devices were characterized by acquiring the dark current density (J)–voltage (V^2) curves under forward bias and the hole mobility was extracted using the Mott-Gurney law, presented in Equation S1:

$$J_D = \frac{9}{8} \epsilon_r \epsilon_0 \mu_h \frac{V^2}{d^3} \quad \#(S1)$$

where J_D is the dark current density, ϵ_r is the relative permittivity of the material, which is ≈ 3 for organic materials, ϵ_0 is vacuum permittivity $8.854 \cdot 10^{-12}$ C V⁻¹ m⁻¹, μ_h is hole mobility, V is the applied bias, and d is the thickness of the HTM layer. The measurement was conducted with a Keithley 2450 Source Measure Unit (SMU) between 0-2 V at scan rate 0.1 V s⁻¹ and a linear fit was applied to data points below 50 mA cm⁻².

Conductivity was assessed by measuring the resistance of HTM-films spin coated on glass substrates with four equally spaced 100 nm thick Au lines evaporated on top as electrodes. Current was sourced through the outer electrodes with a Keithley 2450 source measure unit (SMU) and the voltage drop

between the inner electrodes was measured to calculate resistance R from a linear fit on a voltage (V) –current (I) curve. Conductivity was then calculated using Equation S2:

$$\sigma = \frac{d}{RA} \quad \#(S2)$$

where σ is conductivity of the film, d is the distance between electrodes, and A is the cross-section area through which the current is transmitted.

Photoluminescence studies. A batch of ITO/Perovskite and ITO/HTM/Perovskite samples (with the triple-cation $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ perovskite) was prepared for the photoluminescence studies with TC-HTMs, as well as a Spiro-OMeTAD reference. The same cleaning and spin coating protocols were used as with solar cell fabrication. Steady-state Photoluminescence (PL) spectra were recorded with a FLS1000 spectrofluorometer (Edinburgh Instruments, UK). The time-resolved PL (TRPL) decays were obtained by using a time-correlated single photon counting (TCSPC) apparatus equipped with a PicoHarp 300 controller and a PDL 800-B driver for excitation and a Hamamatsu R3809U-50 microchannel plate photomultiplier for detection in 90° configuration.

Solar cell fabrication. Reagents and solvents aside from the novel HTMs were acquired from standard commercial sources and used as received. Solar cells were fabricated on glass substrates covered with a pre-patterned fluorine-doped tin oxide (FTO) layer (TEC-15, OPV Tech). The substrates were first washed with a 2 % Mucosal detergent solution, rinsed with de-ionized water, and then sequentially sonicated in water, acetone, and 2-propanol for 15 minutes each. Finally, the substrates were dried under nitrogen flow and underwent UV-ozone treatment for 15 minutes before subsequent deposition of the compact titanium dioxide (TiO_2) electron transport layer via spray pyrolysis. Approximately 6 ml of 17.3 vol-% solution of titanium diisopropoxide bis(acetylacetonate) in 2-propanol (diluted from 75 % stock solution, Sigma-Aldrich) was sprayed in 12 passes on substrates heated to 450 °C, followed by 45 minutes of sintering.

A mesoporous TiO₂-layer was then deposited on the cooled down substrates by spin coating 100 µl of titania nanoparticle paste (30NRD, Greatcell solar) dispersed in ethanol (0.15 mg/ml) via static deposition and spin coating at 4000 rpm for 10 s, with a 2 second ramp. The fresh films were immediately annealed on a hotplate at 100 °C for a few minutes and then the batch was heated gradually to 450 °C. After 30 minutes, the substrates were allowed to cool to 200 °C, and swiftly transferred to the inert nitrogen atmosphere of a glovebox for perovskite deposition.

The triple cation CsFAMA perovskite precursor was prepared by first mixing formadanium iodide (FAI, Greatcell solar), methylammonium bromide (MABr, Greatcell solar), lead(II) iodide (PbI₂, TCI), and lead(II) bromide (PbBr₂, TCI) in a 0.95:0.19:1.10:0.20 molar ratio and dissolving them in a mixed 1:4 DMSO:DMF solution. Cesium iodide (CsI, abcr) had been previously dissolved in acetonitrile and was added to the precursor in a 0.06 molar equivalent. The precursor was left stirring overnight before deposition. The perovskite films were formed via the following protocol: 50 µl of the precursor was statically deposited on the substrate. The spin coating program starts with 20s of rotation at 1000 rpm, followed by acceleration to 6000 rpm for 15 seconds. 100 µl of chlorobenzene antisolvent was deposited on the substrate 5s before the end the program. The substrate was then swiftly moved to a hot plate at 110 °C for 1 hour of annealing. The hole transport layers were then formed by dynamically spin coating on top of the cooled down perovskite film 80 µl of HTM solutions in chlorobenzene. The reference Spiro-OMeTAD (Lumtec) solution was prepared in 29.5 mM concentration and doped with 4-tert-Butylpyridine (96 %, Sigma-Aldrich), Li-TFSI (Sigma-Aldrich, pre-dissolved in acetonitrile 520 mg/ml), and FK-209 (Dyename, pre-dissolved in acetonitrile 300 mg/ml) in 3.2, 0.53, and 0.1 molar ratios, respectively. BTC and BTF were tested in different concentrations ranging from 5 mg/ml to 20 mg/ml, and spin coating rotation speeds ranging from 1500-2100 rpm. The results of these tests are shown in Figure S1, with 15 mg/ml and 1800 rpm chosen for BTC in the end. The tBP:Li-TFSI:FK209 doped BTC samples were prepared using similar molar ratios as Spiro-OMeTAD, while F4-TCNQ doping was done in 2 mol-% ratio. To finalize the devices 90-100 nm thick gold electrodes were thermally evaporated on top through a

mask using an OPTIvap Vacuum Deposition Tool (CreaPhys, MBraun) at a vacuum of approximately 5×10^{-6} mbar.

Device characterization. The unencapsulated perovskite solar cells, with an active area of 12/20 mm² were characterized in ambient air. The current density (J)-voltage(V) curves were recorded at a scan rate of 50 mV s⁻¹ using Keithley 2450 SMU (controlled by a measurement program written in MATLAB) for the 20 mm² devices and the Litos Lite system (FLUXiM AG, Switzerland) for 12 mm² devices under air mass 1.5G simulated sunlight (100 mW cm⁻²) with an A++A+A Sinus-70 LED solar simulator from Wavelabs, Germany.

Synthetic procedures. *2'-Bromospiro[cyclohexane-1,9'-fluorene]* (**1**): A mixture of 2-bromofluorene (2.936 g, 11.98 mmol) and tetrabutylammonium bromide (1.328 g, 4.12 mmol) in a 50% NaOH aqueous solution (26 mL) was stirred for 15 min at 60°C. To the red suspension, a solution of 1,5-dibromopentane (2.755 g, 11.98 mmol) in toluene (26 mL) was added and the mixture was kept under overnight stirring. After cooling the solution, the products were extracted with petroleum ether 40-60°C and the organic layer dried over Na₂SO₄. After removing the solvent in vacuo, the crude was purified by flash chromatography (SiO₂, petroleum ether 40-60°C) to afford **1** (2.319 g, 62%) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.76 (d, J = 8.2 Hz, 1H), 7.61 (dd, J = 8.1, 2.2 Hz, 1H), 7.55 (dd, J = 6.7, 1.3 Hz, 1H), 7.42 – 7.31 (m, 3H), 7.28 – 7.23 (m, 1H), 2.14 (m, J = 13.6, 7.4, 4.8 Hz, 2H), 1.89 (m, J = 13.6, 7.5, 4.8 Hz, 2H), 1.80 – 1.69 (m, 2H), 1.67 – 1.56 (m, 2H), 1.56 – 1.46 (m, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 150.9, 149.2, 139.8, 138.5, 132.6, 127.3, 126.7, 123.5, 123.3, 123.1, 122.6, 118.8, 47.8, 34.6, 25.8, 23.5 ppm.

3-Bromo-9-hexyl-9H-carbazole (**2**): A mixture containing 1.5 g (9.00 mmol) of carbazole, and 12 mL of dichloromethane was stirred until completely dissolved and cooled to 0 - 10°C, avoiding light. Then 1.46 g (9.2 mmol) of bromine was added to 3 mL of dichloromethane and the resulting mixture was dropped into the reaction solution. After addition, the temperature of the reaction

solution was increased to 20–30°C. After 0.5 hours, TLC found that the carbazole reaction was complete. 8 mL of saturated salt solution was added to wash the reaction solution and separated. The organic phase was dried with anhydrous sodium sulfate and evaporated to dryness. 2.17 g of 3-bromocarbazole was obtained (98.2% yield). A mixture of 50% aqueous NaOH (6 mL), DMSO (20 mL), and 3-bromocarbazole (2.0 g, 8.16 mmol) was slowly added to 1-bromohexane (1.36, 0.68 mL, 9.80 mmol) at room temperature. The mixture was stirred overnight at 90 °C and cooled to room temperature and then added the brine. The organic phase extracted with dichloromethane was dried over Na₂SO₄. The solvent was removed, and the residue was purified by silica gel column chromatography using petroleum ether as the eluent. 2.02 g of a pale-yellow liquid was obtained (75% yield). ¹H NMR (300 MHz, CDCl₃): δ 8.06 (d, 1H), 7.94 (d, 1H), 7.54 (s, 1H), 7.45 (t, 1H), 7.40 (d, 1H), 7.33 (d, 1H), 7.25 (t, 1H), 4.25 (t, 2H), 1.86 (m, 2H), 1.56-1.23 (m, 6H), 0.88 (t, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 140.6, 139.2, 129.0, 125.9, 125.0, 123.8, 122.6, 121.3, 120.5, 114.1, 111.7, 109.7, 44.6, 31.2, 29.5, 27.0, 22.5, 14.1 ppm.

N-(4-Bromophenyl)-*N*-(4-methoxyphenyl)spiro[cyclohexane-1,9'-fluoren]-2'-amine (**3**): A mixture containing **1** (1.730 g, 5.44 mmol), p-anisidine (0.670 g, 5.44 mmol), palladium acetate (0.061 g, 0.27 mmol), dppf (0.301g, 0.54 mmol) and sodium *tert*-butoxide (1.568 g, 16.32 mmol) in toluene (20 mL) was stirred at 100 °C for 3 hours. Then, under nitrogen flow 1-bromo-4-iodobenzene (1.539 g, 5.44 mmol) was added and the mixture was stirred overnight. After cooling down the reaction to room temperature, toluene was removed under reduced pressure and dichloromethane (50 mL) was added. The obtained mixture was washed with water (3 × 50 mL), the organic layer was collected and dried over Na₂SO₄. Upon removal of the solvent, the crude product was purified by column chromatography (SiO₂, petroleum ether 40-60 °C/CH₂Cl₂ = 3/2 vol/vol) to obtain **3** (1.89 g, yields: 59%) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.79 (d, J = 7.1 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.45 – 7.39 (m, 2H), 7.39 – 7.31 (m, 2H), 7.27 – 7.20 (m, 2H), 7.14 – 7.04 (m, 4H), 6.92 – 6.86 (m, 2H), 6.82 (d, J = 2.3 Hz, 1H), 3.80 (s, 3H), 2.12 (m, J = 13.6, 7.4, 4.8 Hz, 2H), 1.86 (m, J = 13.6, 7.6, 4.8 Hz, 2H), 1.74 (s, 2H), 1.61 (m, J = 13.6, 7.5, 6.4, 4.9 Hz, 2H), 1.56 – 1.46 (m, 2H) ppm.

^{13}C NMR (75 MHz, CDCl_3): δ 159.5, 151.1, 149.1, 146.7, 145.8, 142.6, 138.3, 134.8, 132.2, 127.3, 126.3, 125.1, 124.9, 124.6, 123.1, 122.8, 122.6, 120.0, 114.7, 114.3, 55.3, 47.7, 34.6, 25.8, 23.5 ppm.

N-(4-bromophenyl)-9-hexyl-*N*-(4-methoxyphenyl)-9*H*-carbazol-3-amine (**4**): A mixture containing **2** (1.796 g, 5.44 mmol), *p*-anisidine (0.670 g, 5.44 mmol), palladium acetate (0.061 g, 0.27 mmol), dppf (0.301 g, 0.54 mmol) and sodium *tert*-butoxide (1.568 g, 16.32 mmol) in toluene (20 mL) was stirred at 100 °C for 3 hours. Then, under nitrogen flow 1-bromo-4-iodobenzene (1.539 g, 5.44 mmol) was added and the mixture was stirred overnight. After cooling down the reaction to room temperature, toluene was removed under reduced pressure, and dichloromethane (50 mL) was added. The obtained mixture was washed with water (3 × 50 mL), and the organic layer was collected and dried over Na_2SO_4 . Upon removal of the solvent, the crude product was purified by column chromatography (SiO_2 , petroleum ether 40-60 °C/ CH_2Cl_2 = 3/2 vol/vol) to obtain **4** (1.916 g, yield: 58%) as an off-white solid. ^1H NMR (300 MHz, CDCl_3): δ 8.13 (dd, J = 6.4, 1.4 Hz, 1H), 8.05 (dd, J = 7.9, 1.1 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.52 – 7.46 (m, 2H), 7.45 – 7.35 (m, 2H), 7.30 – 7.22 (m, 3H), 7.11 – 7.03 (m, 3H), 6.88 – 6.82 (m, 2H), 5.50 (m, 1H), 4.25 (t, J = 5.8 Hz, 2H), 3.80 (s, 3H), 1.81 (m, 2H), 1.42 – 1.34 (m, 2H), 1.31 (m, J = 5.5, 2.3 Hz, 4H), 0.94 – 0.85 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 157.5, 142.7, 140.6, 139.7, 136.1, 135.4, 131.7, 130.2, 130.1, 127.5, 125.9, 124.0, 122.7, 122.3, 120.8, 120.7, 120.5, 114.4, 110.4, 109.6, 56.2, 55.3, 44.6, 31.2, 29.5, 27.0, 22.5, 14.1 ppm.

N,N'''-([2,2'-bithiophene]-5,5'-diylbis(4,1-phenylene))bis(*N*-(4-methoxyphenyl)-spiro[cyclohexane-1,9'-fluoren]-2'-amine) (**BTF**): A mixture of **3** (0.510 g, 1.00 mmol), 2,2'-bithiophene (0.083 g, 0.50 mmol), palladium acetate (0.022 g, 0.10 mmol), $\text{P}(o\text{-Anisyl})_3$ (0.070 g, 0.20 mol), pivalic acid (0.030 g, 0.30 mol), Cs_2CO_3 (0.978 g, 3.0 mol) and toluene (5.0 mL) was stirred at 100 °C for 24 hours. After cooling down the reaction to room temperature, toluene was removed under reduced pressure, and dichloromethane (50 mL) was added. The obtained mixture was washed with water (3 × 50 mL), and the organic layer was collected and dried over Na_2SO_4 . Upon removal of the solvent, the crude product was purified by column chromatography (SiO_2 ,

petroleum ether 40-60 °C/CH₂Cl₂ = 1/1 vol/vol) to obtain **BTF** as an orange solid (0.333 g, 65%). ¹H NMR (300 MHz, acetone-d₆): δ 7.79 (d, *J* = 7.1 Hz, 1H), 7.51 (m, 3H), 7.42 – 7.31 (m, 2H), 7.29 – 7.19 (m, 4H), 7.12 – 7.04 (m, 4H), 6.92 – 6.86 (m, 2H), 6.82 (d, *J* = 2.3 Hz, 1H), 3.80 (s, 3H), 2.12 (m, 2H), 1.86 (m, 2H), 1.74 (s, 2H), 1.61 (m, 2H), 1.56 – 1.46 (m, 2H) ppm. ¹³C NMR (75 MHz, acetone-d₆): δ 159.8, 151.1, 149.1, 146.9, 145.7, 143.0, 142.6, 138.3, 138.2, 134.8, 128.2, 128.0, 127.3, 125.1, 125.1, 124.9, 124.6, 124.2, 123.1, 122.8, 122.6, 122.3, 114.7, 114.3, 55.3, 47.5, 34.6, 25.8, 23.5 ppm.

N,N'-([2,2'-bithiophene]-5,5'-diylbis(4,1-phenylene))bis(9-hexyl-*N*-(4-methoxy-phenyl)-9*H*-carbazol-3-amine) (**BTC**): A mixture of **4** (0.607 g, 1.00 mmol), 2,2'-bithiophene (0.083 g, 0.50 mmol), palladium acetate (0.022 g, 0.10 mmol), P(*o*-Anisyl)₃ (0.070 g, 0.20 mol), pivalic acid (0.030 g, 0.30 mol), Cs₂CO₃ (0.978 g, 3.0 mol) and toluene (5.0 mL) was stirred at 100 °C for 24 hours. After cooling down the reaction to room temperature, toluene was removed under reduced pressure, and dichloromethane (50 mL) was added. The obtained mixture was washed with water (3 × 50 mL), and the organic layer was collected and dried over Na₂SO₄. Upon removal of the solvent, the crude product was purified by column chromatography (SiO₂, petroleum ether 40-60 °C/CH₂Cl₂ = 1/1 vol/vol) to obtain **BTC** as a red solid (0.286 g, 54%). ¹H NMR (300 MHz, acetone-d₆) δ 8.22 – 8.13 (m, 2H), 7.94 (dd, *J* = 6.4, 1.5 Hz, 2H), 7.58 (d, *J* = 2.2 Hz, 2H), 7.54 – 7.41 (m, 8H), 7.33 – 7.16 (m, 8H), 7.11 – 7.04 (m, 8H), 6.92 – 6.88 (m, 4H), 4.25 (t, *J* = 5.8 Hz, 4H), 3.80 (s, 6H), 1.81 (m, 4H), 1.49 – 1.22 (m, 12H), 1.00 – 0.77 (m, 6H) ppm. ¹³C NMR (75 MHz, acetone-d₆): δ 159.5, 147.0, 143.0, 142.6, 142.1, 140.3, 138.2, 135.4, 128.2, 128.0, 125.9, 125.1, 124.9, 124.2, 124.2, 123.3, 122.3, 120.6, 120.5, 119.3, 117.4, 114.7, 112.3, 109.6, 55.3, 44.6, 31.2, 29.5, 27.0, 22.5, 14.1 ppm.

Cost evaluation of BTF and BTC.

Reagent	Amount (g)	Amount (mL)	Price (€/g or €/mL)	Total price (€)
2-bromofluorene	2.936		2.865	8.412
1,5-dibromopentane	2.755		0.297	0.818
NaOH (50% w/v)		26.00	0.086	2.236
tetrabutylammonium bromide	1.328		0.939	1.247
Toluene		26.00	0.051	1.326
Silica gel	100		0.037	3.700
Petroleum ether 40-60 °C		450	0.006	2.700
Total cost	20.439 €			
Amount 1	2.319 g			
COST for 1	8.814 €/g			

Reagent	Amount (g)	Amount (mL)	Price (€/g or €/mL)	Total price (€)
2'-bromospiro[cyclohexane-1,9'-fluorene]	1.730		8.814	15.247
p-anisidine	0.670		6.260	4.190
Pd(AcO) ₂	0.061		91.020	5.552
dppf	0.301		23.520	7.079
^t BuONa	1.568		0.441	0.691
1-bromo-4-iodobenzene	1.539		6.120	9.419
Toluene		20.00	0.051	1.020
Silica gel	100.00		0.037	3.700
Petroleum ether 40-60 °C		300.00	0.006	1.800
Methylene chloride		250.00	0.008	2.000
Total cost	50.698 €			
Amount intermediate 2	1.892 g			
COST for intermediate 2	26.796 €/g			

Reagent	Amount (g)	Amount (mL)	Price (€/g or €/mL)	Total price (€)
3	0.510		26.796	13.666
2,2'-bithiophene	0.083		19.500	1.618
Pd(AcO) ₂	0.022		91.020	2.002
P(o-Anisyl) ₃	0.070		32.600	2.280
pivalic acid	0.030		0.135	0.004
Cs ₂ CO ₃	0.978		1.054	1.031
Toluene		5.00	0.051	0.255
Silica gel	100.00		0.037	3.700
Petroleum ether 40-60 °C		200.00	0.006	1.200
Methylene chloride		350.00	0.008	2.800
Total cost	28.556 €			
Amount BTF	0.333 g			
COST for BTF	85.754 €/g			

Reagent	Amount (g)	Amount (mL)	Price (€/g or €/mL)	Total price (€)
Carbazole	1.500		0.320	0.481
Methylene chloride		15.00	0.008	0.120
Bromine	1.460		0.326	0.516
Total cost			1.170 €	
Amount 3-bromo-9H-carbazole			2.170 g	
COST for 3-bromo-9H-carbazole			0.515 €/g	

Reagent	Amount (g)	Amount (mL)	Price (€/g or €/mL)	Total price (€)
3-bromo-9H-carbazole	2.000		0.515	1.029
1-bromohexane		1.36	0.222	0.356
NaOH (50% w/v)		6.00	0.086	0.516
DMSO		20.00	0.106	2.123
Silica gel	100		0.037	3.700
Petroleum ether 40-60 °C		450	0.006	2.700
Total cost			10.424 €	
Amount 2			2.020 g	
COST for 2			5.161 €/g	

Reagent	Amount (g)	Amount (mL)	Price (€/g or €/mL)	Total price (€)
2	1.796		5.161	9.268
<i>p</i> -anisidine	0.670		6.260	4.190
Pd(AcO) ₂	0.061		91.020	5.552
dppf	0.301		23.520	7.079
^t BuONa	1.568		0.441	0.691
1-bromo-4-iodobenzene	1.539		6.120	9.419
Toluene		20.00	0.051	1.020
Silica gel	100.00		0.037	3.700
Petroleum ether 40-60 °C		300.00	0.006	1.800
Methylene chloride		250.00	0.008	2.000
Total cost			44.719 €	
Amount 4			1.916 g	
COST for 4			23.340 €/g	

Reagent	Amount (g)	Amount (mL)	Price (€/g or €/mL)	Total price (€)
4	0.607		23.340	14.167
2,2'-bithiophene	0.083		19.500	1.618
Pd(AcO) ₂	0.022		91.020	2.002
P(<i>o</i> -Anisyl) ₃	0.070		32.600	2.280
pivalic acid	0.030		0.135	0.004
Cs ₂ CO ₃	0.978		1.054	1.031
Toluene		5.00	0.051	0.255
Silica gel	100.00		0.037	3.700
Petroleum ether 40-60 °C		200.00	0.006	1.200
Methylene chloride		350.00	0.008	2.800
Total cost			29.057 €	
Amount BTC			0.286 g	
COST for BTC			101.599 €/g	

Transition	Probability	Energy (eV)	Wavelength (nm)	Osc. Strength
BTF				
H→L	100%	2.57	481.9	2.03
H→L+2	66%	3.38	366.7	0.52
H-2→L	72%	3.51	353.3	0.41
BTC				
H→L	100%	2.56	483.6	2.01
H-2→L	83%	3.47	356.8	0.38
H→L+4	82%	3.82	324.9	0.24

Table S1 Energy, oscillator strength, and composition of the main vertical electronic transitions of **BTF** and **BTC**.

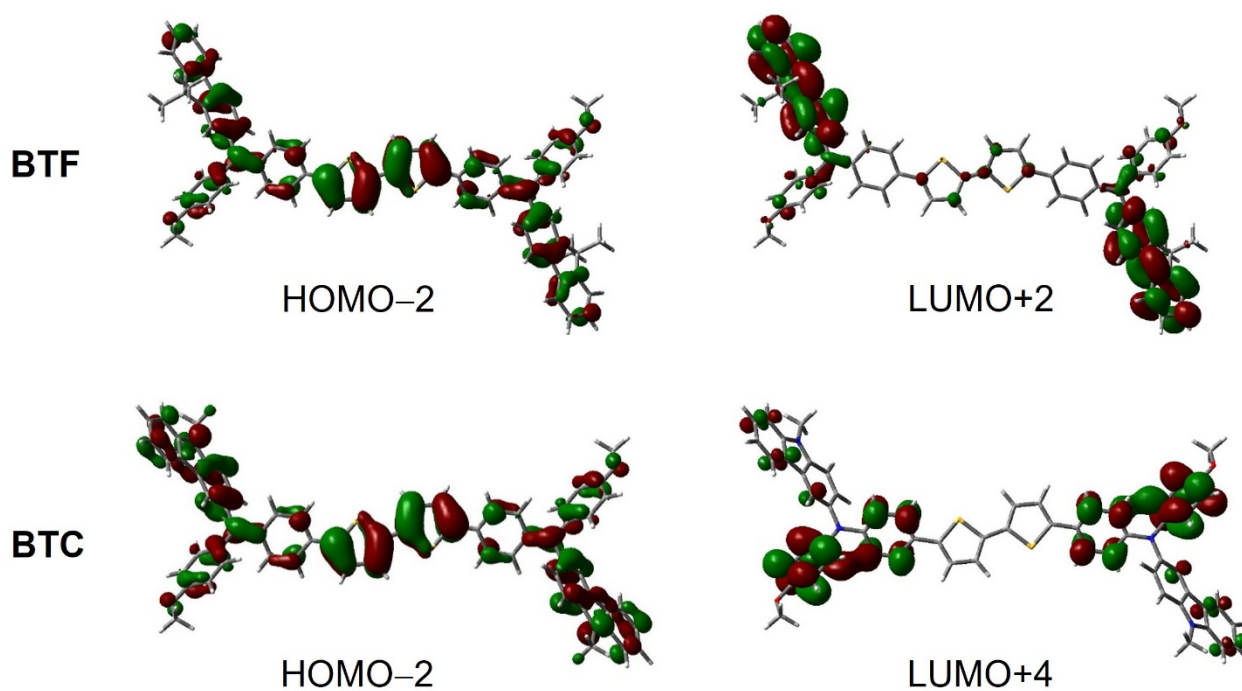


Fig. S1 Isodensity surfaces ($0.02 \text{ e}/\text{\AA}^3$) of the selected molecular orbitals of **BTF** and **BTC** involved in the electronic transitions reported in Table S1.

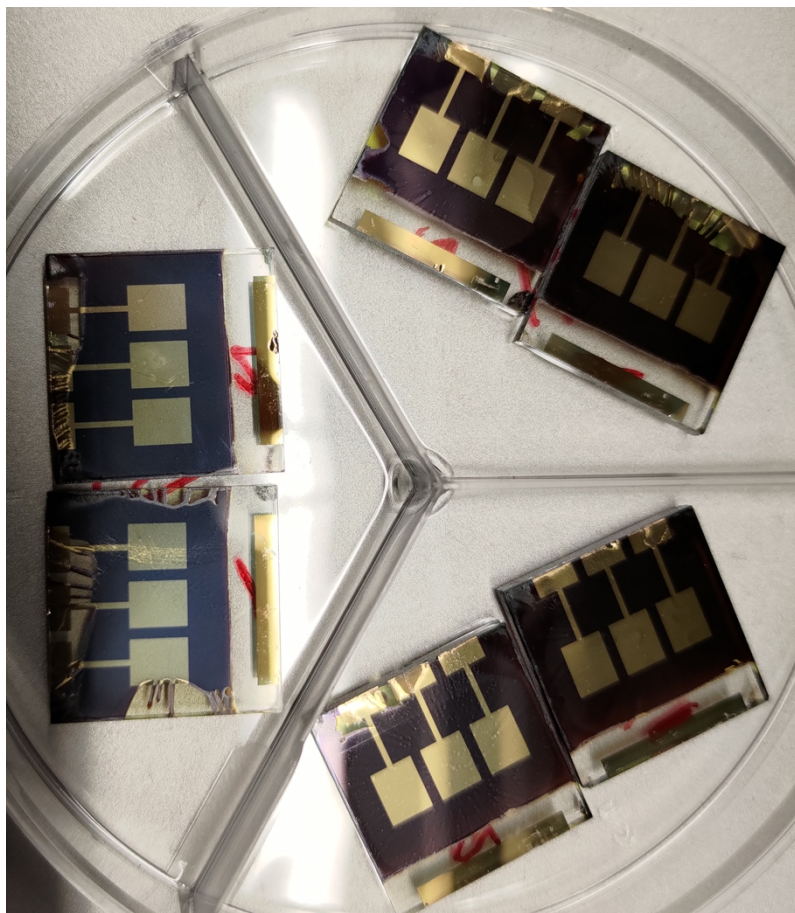


Fig. S2 Pictures of the PSCs employing **BTF**, **BTC**, and **Spiro-OMeTAD** as the HTM.

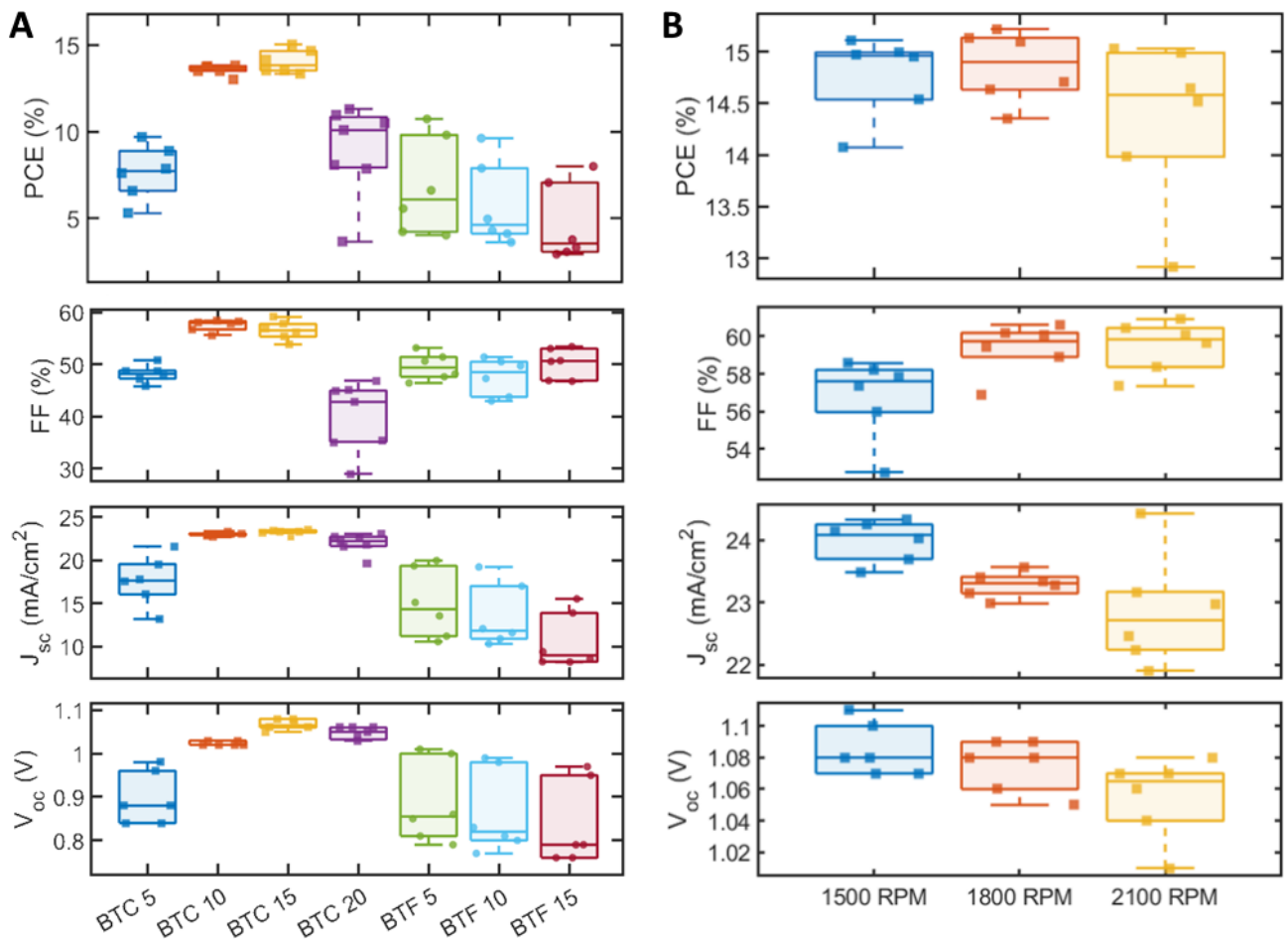


Fig. S3 A) Figures of merit of solar cell samples employing **BTC** and **BTF** at concentrations ranging from 5-20 mg/ml. B) **BTC**-based solar cells with the hole transport layer dynamically spin coated at different speeds.

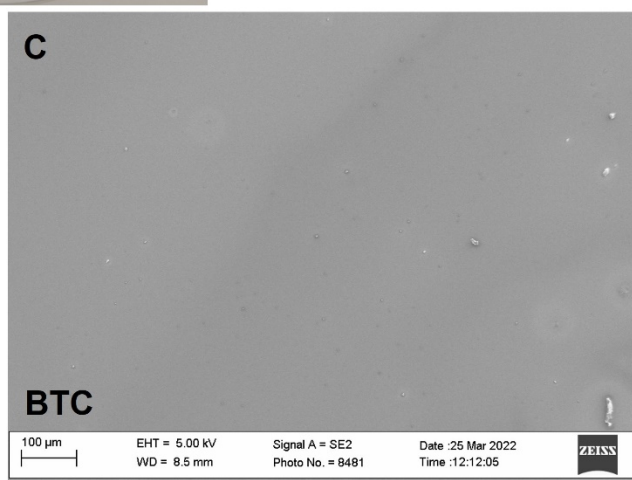
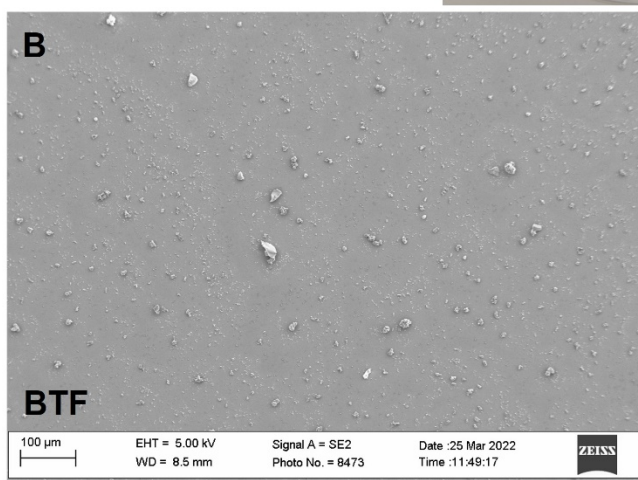
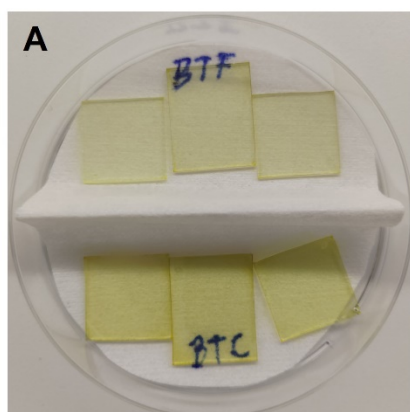


Fig. S4 A) Photographs of the **BTF** and **BTC** films deposited on quartz. SEM analysis of the **BTF** (B) and **BTC** (C) films.

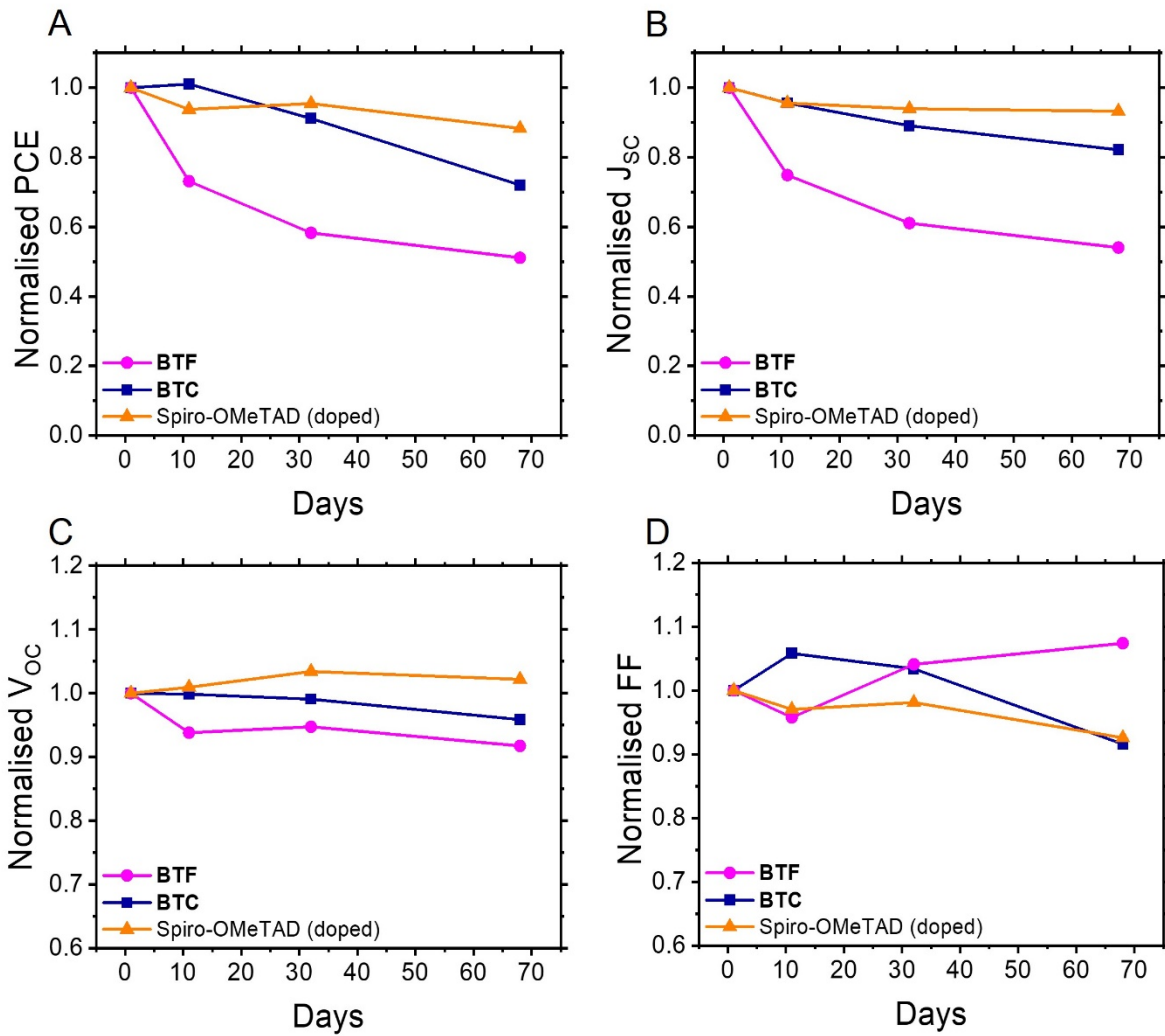


Fig S5 Evolution over time of the normalized figures of merit in undoped **BTF**- and **BTC**-based PSCs in comparison to doped Spiro-OMeTAD benchmark: A) power conversion efficiency, B) short-circuit current density, C) open circuit voltage, and D) fill factor.

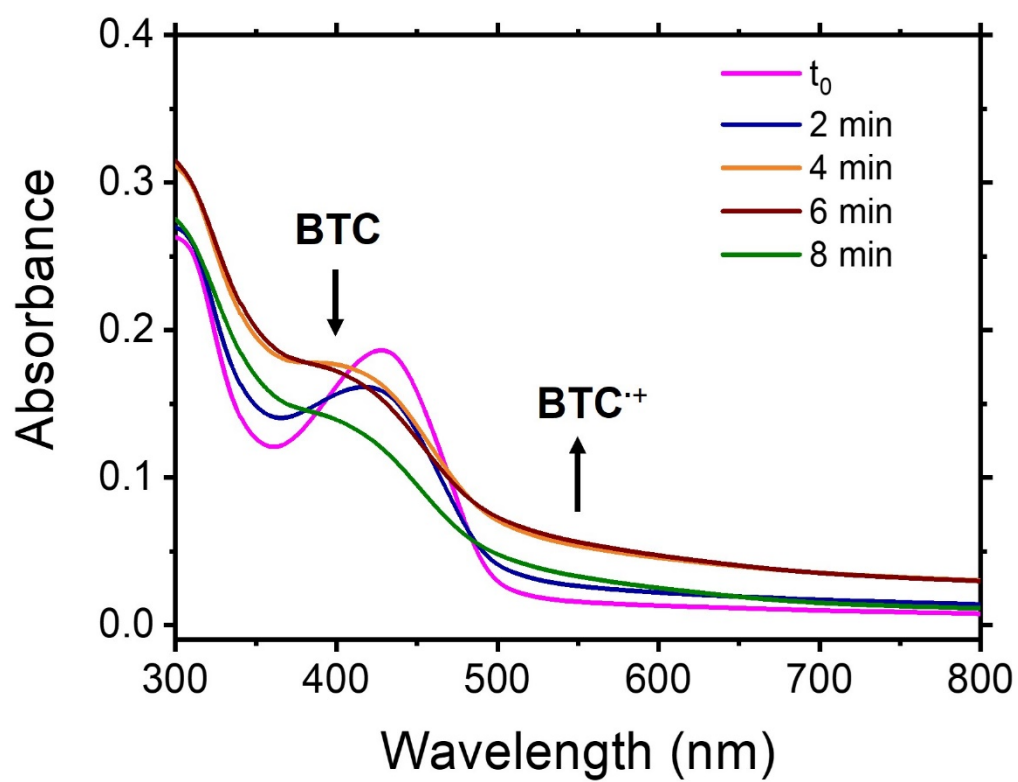


Fig S6 Evolution over time of the **BTC** absorption profile in chloroform upon irradiation.

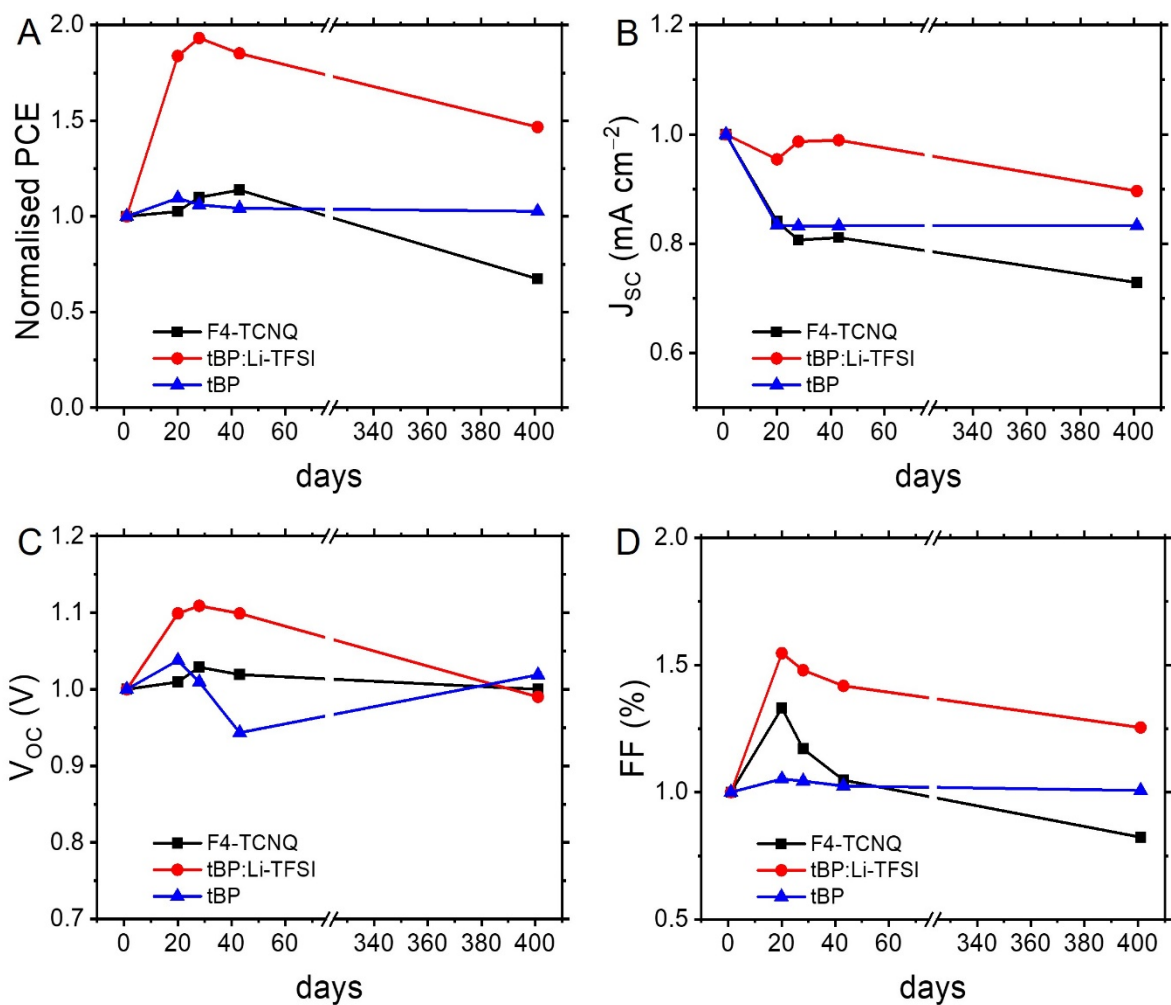


Fig S7 Evolution over time of the normalized figures of merit in doped **BTC**-based PSCs: A) power conversion efficiency, B) short-circuit current density, C) open circuit voltage, and D) fill factor.

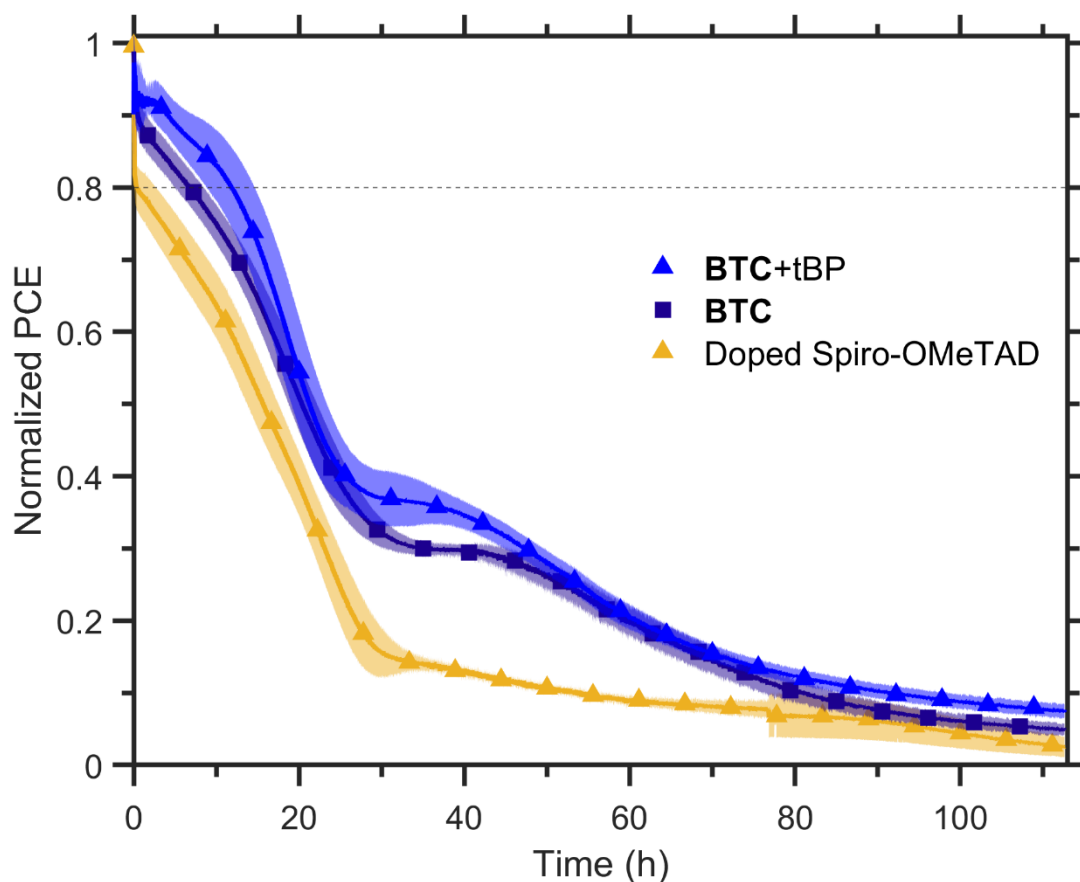


Fig. S8 The mean values obtained from maximum power point tracking of 8 pixels of each sample type. The shaded area represents the standard deviation at each point. The measurements were performed in inert nitrogen atmosphere under continuous 65 °C heating and 1-sun illumination.