

Supporting Information for

Subphthalocyanine-based electron transporting materials for perovskite solar cells.

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1. Instrumentation and materials

Nuclear magnetic resonance spectra (^1H -, ^{19}F -, ^{11}B -NMR) were recorded on a Bruker AV-300 Bruker DRX-500 spectrometers in the Interdepartmental Investigation Service of UAM. Deuterated solvent employed in each case is indicated in brackets, and its residual peak was used to calibrate the spectra using literature reference δ ppm values.ⁱ All the experiments were recorded at room temperature.

High-resolution mass spectra (HRMS) were recorded in the Interdepartmental Investigation Service of UAM employing Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight (MALDI-TOF), using a Bruker-Ultraflex-III spectrometer with a Nd:YAG laser operating at 355 nm, for MALDI-TOF. The matrixes and internal references employed are indicated for each spectrum. Infrared Spectra were recorder in solid state on a Bruker Vector 22 spectrophotometer.

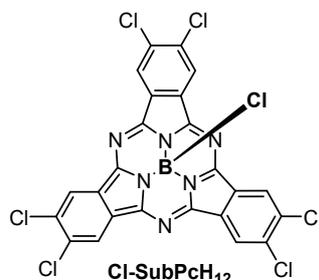
Ultraviolet and visible (UV-Vis) spectra were recorded using solvents in the spectroscopic grade in the Organic Chemistry Department of UAM employing a JASCO-V660 spectrophotometer. The logarithm of the molar extinction coefficient (ϵ) is indicated in brackets for each maximum. Likewise, fluorescence measurements were carried out with a JASCO-V8600 spectrofluorometer.

Electrochemical measurements were performed on an Autolab PGStat 30 equipment using a three-electrode configuration system. The measurements were carried out using freshly distilled THF solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) and a concentration of approximately 10⁻⁴ M of the corresponding compound. A glassy carbon electrode (3 mm diameter) was used as the working electrode, and a platinum wire and an Ag/AgNO₃ (in CH₃CN) electrode were employed as the counter and the reference electrodes, respectively. Ferrocene (Fc) was used as external reference and all the potentials were given relative to the Fc/Fc⁺ couple. Scan rate was 100 mV.s⁻¹. HOMO and LUMO level were calculated using the equation [$E_{LUMO} = -5.1 - E_{1/2red}$ (vs. Fc/Fc⁺) (eV)] and the optical band gap [$E_{HOMO} = E_{LUMO} + E_{g,opt}$ (eV)].

The monitoring of the reactions has been carried out by thin layer chromatography (TLC), employing aluminium sheets coated with silica gel type 60 F254 (0.2 mm thick, Merck). The analysis of the TLCs was carried out with an UV lamp of 254 and 365 nm. Purification and separation of the synthesized products was performed by normal-phase column chromatography, using silica gel (230-400 mesh, 0.040-0.063 mm, Merck).

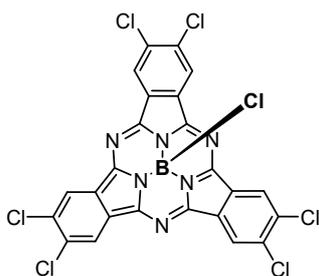
Chemicals were purchased from commercial suppliers and used without further purification. Dry solvents were purchased from commercial suppliers in anhydrous grade or thoroughly dried before use employing standard methods. Solid, hygroscopic reagents were dried in a vacuum oven before use.

The characterization of **Cl-SubPcCl₆** have been previously reported.ⁱⁱ



2. Synthetic Procedures and Compound Data

Cl-SubPcCl₆



In a 50 mL two-necked round-bottomed flask, equipped with a condenser, magnetic stirrer and rubber seal, a 1.0 M solution of BCl_3 in *p*-xylene (1.25 mL) was added to 4,5-dichlorophthalonitrile (426 mg, 1.25 mmol) in 15 mL *o*-DCB under argon atmosphere. The reaction mixture was stirred at 180 °C reflux for 24 h. The purple solution was allowed to cool to room temperature and flushed with argon. The dark purple reaction slurry was dissolved in toluene/THF 10:1 and passed through a short silica plug. The solvent was removed by vacuum distillation and the resulting dark solid was subjected to column chromatography on silica gel using toluene as an eluent. By washing with methanol, 180 mg (0.28 mmol) of Cl-SubPcCl₆ were obtained as a purple-gold solid. Yield: 68%; **Mp** > 250 °C. **¹H-NMR** (300 MHz, CDCl_3): δ (ppm) = 8.95 (s, 6H).; **¹¹B-NMR** (160.5 MHz, CDCl_3): δ (ppm) = -13.8 (s).; **¹³C-NMR** (75.5 MHz, CDCl_3): 148.9, 135.5, 129.8, 124.1.; MS (MALDI-TOF, DCTB) HRLSI-MS: m/z Calcd for $[\text{C}_{24}\text{H}_6\text{BCl}_7\text{N}_6]$: 633.8537; Found: 633.8556.

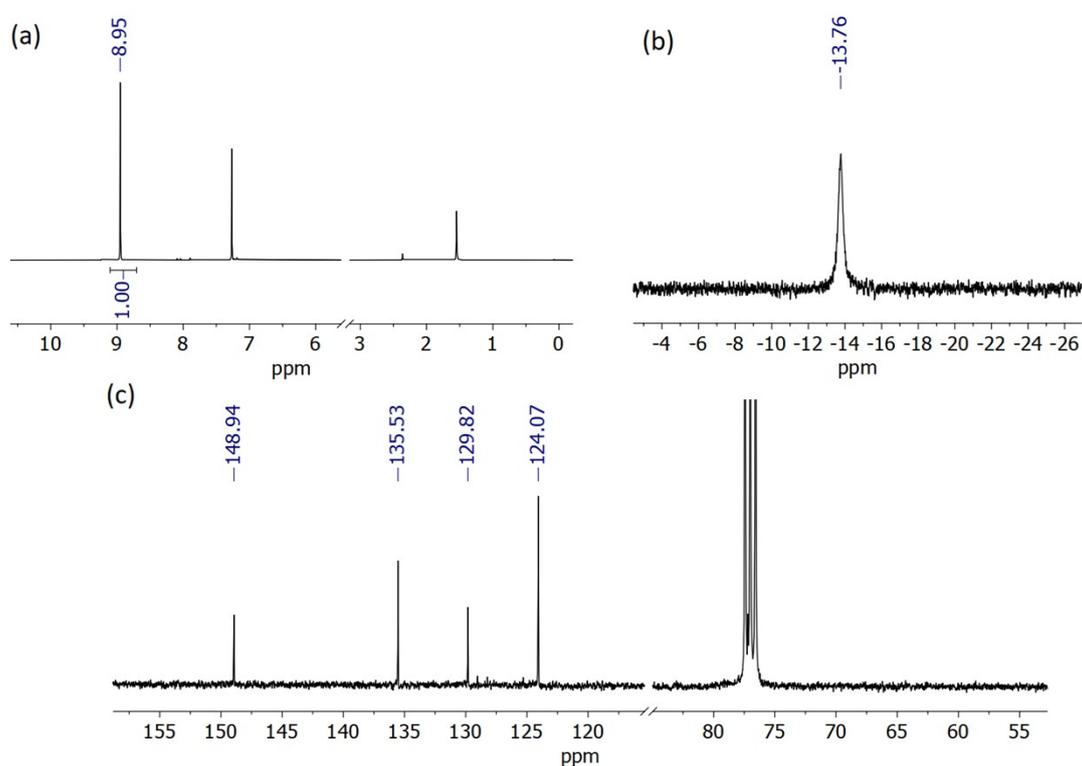


Figure S1. a) ¹H-, b) ¹¹B- and c) ¹³C-NMR spectra of Cl-SubPcCl₆ in CDCl_3

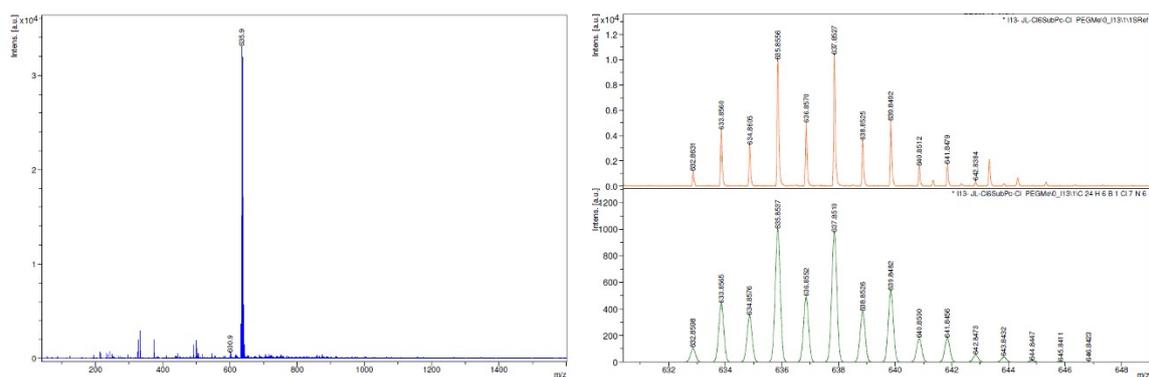


Figure S2. Mass spectrum of **Cl-SubPcCl₆**

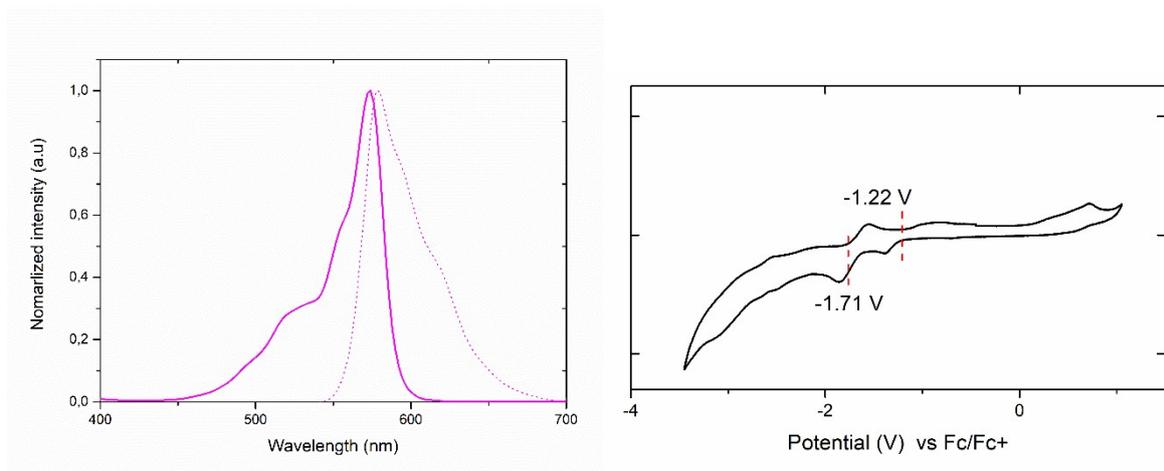
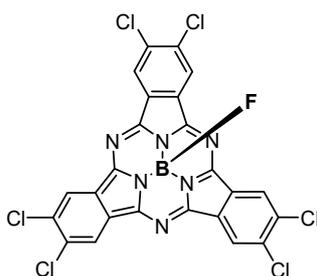


Figure S3. UV/Vis absorption and emission of **Cl-SubPcCl₆** (left) and cyclic voltammogram (right) (V vs. ferrocene/ferrocenium ion couple) of **Cl-SubPcCl₆** in THF. Supporting electrolyte, Bu₄NPF₆ (0.10 M); working electrode, glassy carbon; counter electrode, platinum wire; reference electrode, Ag/AgNO₃. Optical band-gap of ($E_{g,opt}(eV)$) **Cl-SubPcCl₆** = 2.16 eV.

F-SubPcCl₆



In a 25 mL two-necked round-bottomed flask, equipped with a condenser, magnetic stirrer, and rubber seal, **Cl-SubPcCl₆** (300 mg, 0.40 mmol) was dissolved in dry toluene (4 mL) under argon atmosphere. Boron trifluoride diethyl etherate (Et₂O·BF₃, 1.3 mL, 25 molar equiv) was added dropwise. The reaction mixture was stirred at 120 °C for 12 h. The purple solution was allowed to cool to room temperature and pyridine was added dropwise until the color of the reaction returned to a characteristic SubPc pink color. The flask was placed in an ice bath for one hour, and the precipitate subsequently isolated by vacuum filtration. The filter cake was rinsed with methanol followed by ether to give 232 mg (0.37 mmol) of compound **F-SubPcCl₆** as a purple solid. Yield: 94%; **Mp** > 250 °C. ¹H-NMR (300 MHz, C₂D₂Cl₄, 120 °C): δ (ppm) = 8.95 (s, 6H). ¹⁹F-NMR (470 MHz, C₂D₂Cl₄, 120 °C): δ (ppm) = -156.3 (q, J = 28.5 Hz,

1F; B-F). ^{11}B -NMR (160.5 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 120 °C): δ (ppm) = -14.1 (d, J = 28.5 Hz, 1B; B-F); MS (MALDI-TOF, DCTB): HRLSI-MS: m/z Calcd for $[\text{C}_{24}\text{H}_6\text{BCl}_6\text{FN}_6]$: 619.8833; Found: 619.8843.

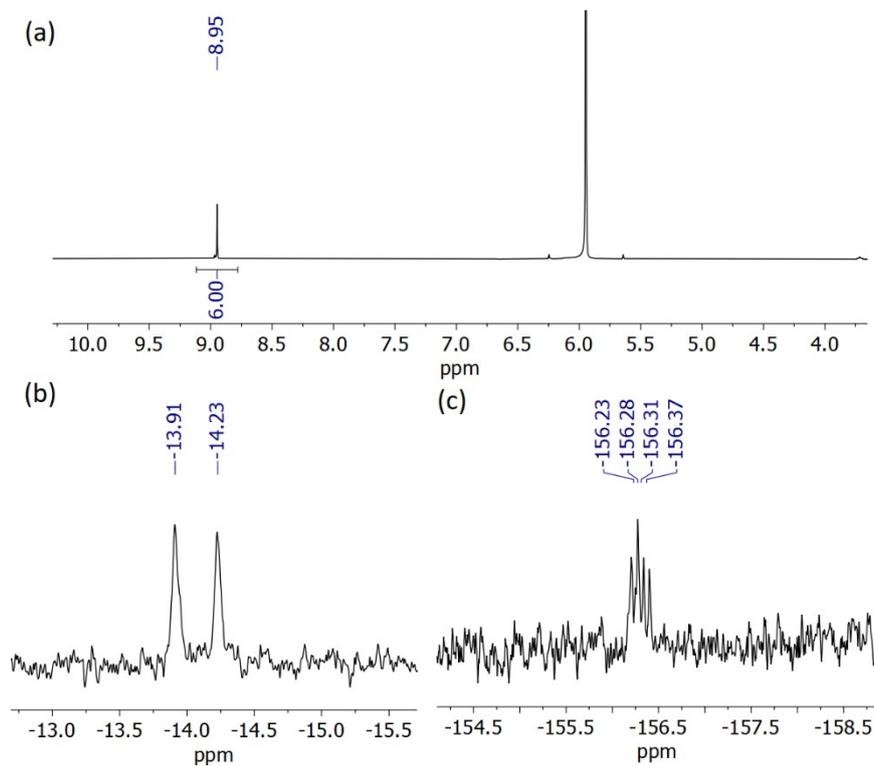


Figure S4. a) ^1H -, b) ^{11}B - and c) ^{19}F -NMR spectra of F-SubPcCl_6 in $\text{C}_2\text{D}_2\text{Cl}_2$ at 120 °C

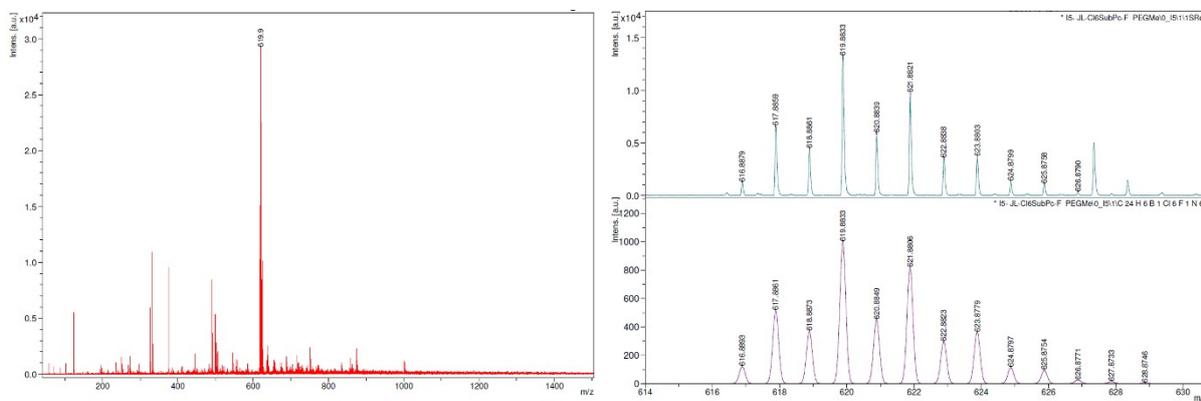


Figure S5. Mass spectrum of F-SubPcCl_6

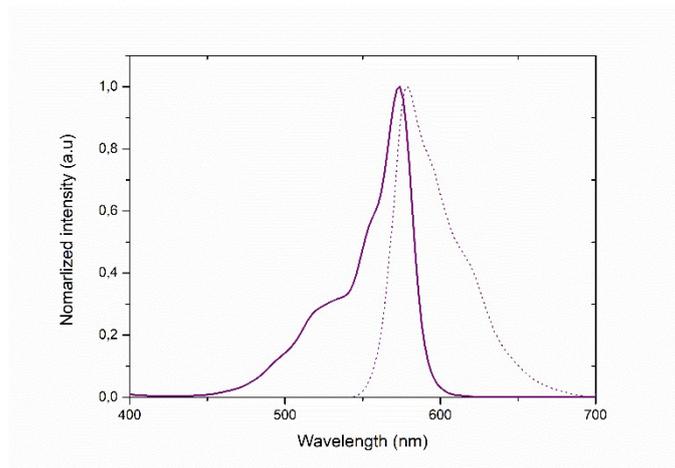


Figure S6. UV/Vis absorption and emission of **F-SubPcCl₆** in THF.

3. Experimental section of device fabrication and characterization.

Thin-film perovskite and solar cell fabrication

Laser-etched fluorine-doped tin oxide (FTO)-coated glass substrates (TEC-15AX, NSG group) were cleaned by a sequential sonication treatment (10 min each) in a 2% Helmanex solution, water, deionized water and isopropanol. Then, the clean FTO substrates were exposed to an ultraviolet-O₃ treatment for 30 min.

A NiO_x compact layer was deposited in air by spray pyrolysis deposition (SPD) method using a diluted solution of Nickel acetate acetylacetonate in acetonitrile (0.04 mol/L solution).¹ The film fabrication was carried out at 550 °C and the samples were kept on the hot plate until the substrate temperature reached room temperature. After the NiO_x deposition, an ultraviolet-O₃ treatment for 30 min was performed to enhanced the PTAA wetting in the sample and the samples were transferred to a MBraun glovebox (, <0.1 ppm H₂O, <0.1 ppm O₂). A thin film of PTAA was deposited from a 0.5 mg/mL solution in toluene, spin-coated at 4,000 r.p.m for 30 s and annealed at 100°C for 10 min.

Solution-processed perovskite preparation

Solution-processed CsFAMAPbIBr perovskite layers were deposited on the FTO/NiO_x/PTAA samples. The [(FAPbI₃)_{0.87}(MAPbBr₃)_{0.13}]_{0.92}(CsPbI₃)_{0.08} perovskite solution was prepared by dissolving 17.41 mg MABr, 27.02 mg CsI, 57.06 mg PbBr₂, 178.94 mg FAI and 548.60 mg PbI₂ in 1 ml of DMF:DMSO mixture (0.78:0.22 v/v). Then, the perovskite layer was prepared by spin coating at 2,000 r.p.m. for 10 s, followed by 5,000 r.p.m. for 30 s. During spinning in the second step, 110 μl of chlorobenzene (antisolvent) was dropped on the sample at the 15 s before finishing the process. The samples were annealed at 100°C for 1 h in an inert atmosphere. Once the samples were cooled down, 100 μL of PEAI (2 mg/mL in isopropanol) was added to the CsFAMAPbIBr during spinning at 5,000 r.p.m and the samples were annealed at 110°C for 30 min in an inert atmosphere.

Vacuum-processed perovskite preparation

The prepared HTM layers were then transferred to the PRO Line PVD 75 vacuum chamber from Kurt J. Lesker Company equipped with four thermally-controlled sources. The ceramic crucibles were filled with the perovskite precursors, methylammonium iodide (MAI) and PbI₂, and heated up until the respectively sublimation temperatures of ~120°C for MAI and ~240°C for PbI₂ at a vacuum pressure of ~1 · 10⁻⁶ mbar. During the perovskite deposition, the deposition rate of each precursor was kept constant

at 3.6 and 0.6 Å/s and monitored by independent quartz microbalance crystal sensors (QCMs). The substrates were kept at a rotation of 5 r.p.m. at room temperature during the perovskite deposition. Prior to the perovskite deposition, individual calibration of each precursors was carried out by calibrating the actual perovskite thickness measured by profilometer with the measured thickness monitored by the individual QCM. No thermal annealing during or post perovskite deposition was needed in the fabrication of the vacuum-deposited perovskite layers.

Once the solution- or vacuum-processed perovskite layer was deposited, thin films of SubPc were deposited by thermal evaporation at a deposition rate of 0.1 Å/s at ~240°C. Prior to its implementation into the PSCs, individual calibration was performed by calibrating the actual perovskite thickness measured by profilometer with the measured thickness monitored by the individual QCM. After the desired SubPc thickness was deposited (2, 5 or 10 nm), 20 nm of C₆₀ (Sigma-Aldrich, 99.9%) followed by 3 nm of bathocuproine (BCP, Sigma-Aldrich, 99.9%) was thermally evaporated. As top electrode, 1 nm Cr and 70 nm Au were deposited by thermal evaporation.

Thin-film perovskite and solar cell characterization

The thin-film absorbance spectra were recorded with a Lambda 950S spectrophotometer (PerkinElmer, Inc.). The steady-state photoluminescence spectra of the glass/perovskite and glass/perovskite/SubPc thin films were measured and recorded using Fluorolog3-22 spectrofluorometer. The spectra were recorded upon excitation at 475 nm with the sample illuminated from front side (perovskite or HTM side). Time-resolved PL spectroscopy was conducted by Fluorolog TCSPC with an excitation wavelength of 640 nm and detection wavelength of 780 nm (HORIBA, Ltd.). The measurements were carried out at the low excitation fluence of 1.4 10⁻¹⁵ cm⁻³. The TrPL decays were fitted to a double exponential equation.

The $J - V$ characteristics of the solution- and vacuum-processed PSCs were measured by using a 2400 Keithley system (scan rate: 50 mV s⁻¹ and 10 mV voltage step for reverse and forward bias) in combination with a Xe-lamp Oriel sol3A sun simulator (Newport Corporation), previously calibrated to AM1.5G standard conditions by using the reference cell Oriel 91150 V. The devices were measured without light soaking and the illumination area was defined through a shadow mask of 16 mm². For each device condition, eight devices were fabricated and characterized. The stability test was performed as maximum power tracking under 100 mW cm⁻² illumination with the Xe-lamp Oriel sol3A sun simulator (Newport Corporation). EQE was measured with IQE200B Quantum Efficiency Measurement System (Oriel, Newport). No anti-reflective coating was applied and the devices were measured without encapsulation. Scanning electron microscopy (SEM) images were recorded by in-lens detector of FEI Teneo Schottky Field Emission SEM at tension of 2 kV (surface images) and 5 kV (cross section images).

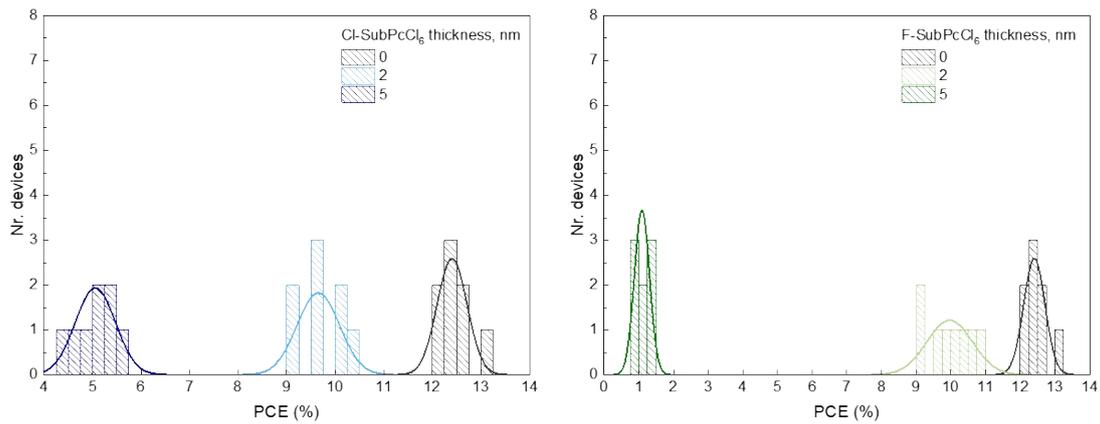


Figure S7. PCE distribution of solution-processed *p-i-n* solar cells containing a) 2 and 5 nm of Cl-SubPcCl₆ and b) 2 and 5 nm of F-SubPcCl₆. PCE distribution of reference samples (w/o subphthalocyanine layer) are also presented for comparison.

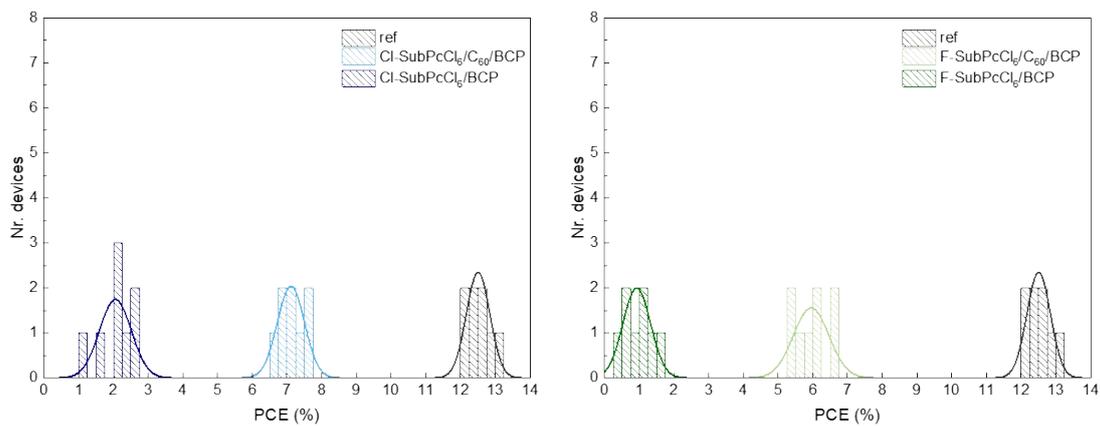


Figure S8. PCE distribution of vacuum-processed *p-i-n* solar cells a) with or without C₆₀ layer in Cl-SubPcCl₆/BCP as ETM and b) with or without C₆₀ layer in Cl-SubPcCl₆/BCP as ETM. PCE distribution of reference samples (w/o subphthalocyanine layer) are also presented for comparison.

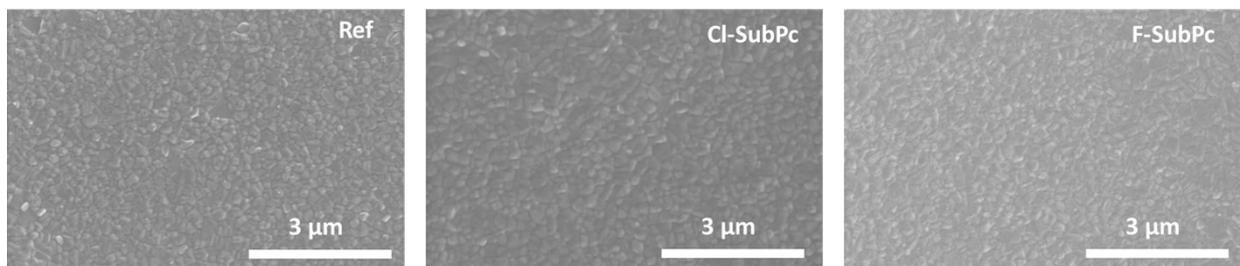


Figure S9. Top-view scanning electron images (SEM) of solution-processed perovskite layers without SubPc (ref) or with 5 nm Cl-SubPcCl₆ (Cl-SubPc) or 5 nm F-SubPcCl₆ (F-SubPc) layers, respectively.

Table S1. Fitting parameters of the time-resolved photoluminescence decays.

	t_1' ns	t_2' ns
CsFAMAPbIBr	52.8	149.9
CsFAMAPbIBr/F-SubPcCl ₆	38.2	128.5
CsFAMAPbIBr/Cl-SubPcCl ₆	45.0	154.5
MAPI	23.9	87.0
MAPI/F-SubPcCl ₆	5.0	37.8
MAPI/Cl-SubPcCl ₆	3.2	27.0

4. References

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- [i] N. R. Babij, E. O. McCusker, G. T. Whiteker, B. Canturk, N. Choy, L. C. Creemer, C. V. D. Amicis, N. M. Hewlett, P. L. Johnson, J. A. Knobelsdorf, F. Li, B. A. Lorsbach, B. M. Nugent, S. J. Ryan, M. R. Smith and Q. Yang, *Org. Process Res. Dev.*, 2016, **20**, 661.
- [ii] C. Duan, G. Zango, M. Garcia Iglesias, F. J. M. Colberts, M. M. Wienk, M. V. Martinez-Diaz, R. A. J. Janssen and T. Torres, *Angew. Chem., Int. Ed.*, 2017, **56**, 148.