Supporting Information

Anchoring Vertical Dipole to Enable Efficient Charge Extraction for High Performance Perovskite Solar Cells

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Experimental Section

Materials: ITO glass were purchased from Advanced Election Technology (China). SnO$_2$ were purchased from Alfa Aesar. Spiro-OMeTAD, Formamidinium Iodide (FAI), Methylammonium Bromide (MABr), Methylammonium Chloride (MACl) and Lithium-bis (trifluoromethanesulfonyl) imide (Li-TFSI) were purchased from Xi’an Polymer Light Technology Corp (Xi’an p-OLED). Lead (II) iodide PbI$_2$ were purchased from Advanced Election Technology (China). N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), chlorobenzene (CB), isopropyl alcohol (IPA), acetonitrile (ACN) and Ethanol purchased from Sigma-Aldrich. Gold (Au, 99.99%) were obtained from commercial sources.

Solution Preparation: SnO$_2$ colloid solution (15 wt %) was diluted within DI water (1:5.5, v: v), and stirring at room temperature for 10 min, followed use a syringe and an aqueous filter to filter the above solution. The preparation of PbI$_2$ precursor solution, 599.3 mg PbI$_2$ powder was dissolved in 1mL DMF/DMSO 950:50 and stirred overnight at 70 °C. The preparation of the solution of organic amine salts , an isopropyl alcohol (IPA) solution containing organic salts (the mass ratio of FAI: MABr: MACl is 60 mg:6 mg: 6 mg), and stirred at 70 °C for 30 min. The preparation of the solution of Spiro-OMeTAD HTL, which consisted of 72.3 mg spiro-OMeTAD, 28.8 μL 4-tertbutylpyridine, 17.5 μL lithium-bis (trifluoromethanesulfonyl) imide (Li-TFSI) solution (520 mg Li-TFSI in 1 mL acetonitrile), and 1 mL chlorobenzene. The preparation of organic-inorganic (OI) complexes solution, 1mg CL-CH$_3$, CL-CF$_3$ powder was dissolved in 1mL ethanol and stirred at room temperature.

Device Fabrication: The glass/ITO substrate was first scrubbed in detergent, and then sequentially cleaned by sonication in deionized water, acetone, and isopropanol for 25 minutes, respectively. After that, nitrogen dried glass/ITO were treated with plasma for 5 min before usage. Then deposit SnO$_2$ on the substrate as an electron transport layer by spin-coated at 3500 rpm for 30 s and annealed in ambient air at 150 °C for 30 min on the hot plate. After cooling to room temperature, the substrates were transferred to a nitrogen filled glove box. Then, 1.3M of PbI$_2$ dissolved in anhydrous DMF: DMSO 95:5(v:v) was spin coated onto SnO$_2$ at 2000 rpm for 30 s, and heating at 70 °C for 1 min and cooling 10 min, followed the mixture solution of FAI: MABr: MACl (60 mg:6 mg :6 mg in 1 mL IPA) was spin-coating onto the PbI$_2$, at 3000 rpm for 30 s, then transferred into dry air (10-20 RH%) filled glove box annealed at 150 °C for 10 min on the hot plate. After the substrates were transferred to a nitrogen filled glove box, cooling to room temperature. The dissolved CL-CH$_3$ and CL-CF$_3$ are spin-coated on the surface of the perovskite at 4000 rpm for 30 s. Subsequently, the substrate transferred into nitrogen filled glove box was deposited on the perovskite films as the hole transport layer by spin-casting the Spiro-OMeTAD solution at 4000 rpm for 30 s. Finally, an approximate 80 nm thick of Au electrode was fabricated using a shadow mask under high vacuum by thermal evaporation.

Density functional theory Methodology: Density functional theory (DFT) calculations were performed utilizing the Vienna Ab-initio Simulation Package (VASP) code with the projector augmented wave method (PAW). The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was chosen for electron exchange and correlation. Energy cutoff, energy and force convergence criteria
were set at 450 eV, $10^{-5}$ eV, and 0.02 eV Å$^{-1}$ respectively in all calculations. We used a 2$\times$2$\times$1 gamma centered k-point grid generated by the Monkhorst-Pack scheme for two passivation models of FAPbI$_3$ (001) surface structures (368 atoms) passivated by CL-CH$_3$ and CL-CF$_3$ molecules. All electrostatic potential (ESP) of molecules was calculated based on all-electron double-$\xi$ valence basis sets of LanL2DZ.

Characterizations: The crystal structure and phase of the perovskite were characterized using X-ray diffraction spectrometer were obtained on Bruker Advanced D8 X-ray diffractometer using Cu Kα ($\lambda = 0.154$ nm) radiation. A UV-Vis spectrophotometer (Agilent Cary 5000) was used to collect the absorbance spectra of the perovskite films. Steady state photoluminescence (PL) spectra were recorded on Shimadzu RF-5301pc. Time-resolved photoluminescence spectra were measured on a PL system (Fluo-Time 300) under excitation with a picosecond pulsed diode laser with a repetition frequency of 1 MHz. The morphology of the films was studied by field-emission scanning electron microscopy (SEM; TESCAM MIRA3). The surface potential of perovskite films obtained with a atomic force microscopy (AFM; Asylum Research MFP-3D-Stand Alone). An FEI Helios Nanolab 600i dual beam, focus ion beam/field emission gun-scanning electron microscope (FIB/FEGSEM) (FEI, Netherland), was used to prepare the device cross-section for scanning transmission electronic microscopy (STEM) imaging and analysis (FEI, Netherland). X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo ScientificTM K-AlphaTM+ spectrometer equipped with a monochromatic Al Kα X-ray source (1486.6 eV) operating at 100 W. Samples were analyzed under vacuum (P < 10$^{-8}$ mbar) with a pass energy of 150 eV (survey scans) or 50eV (high-resolution scans). The XPS spectra were calibrated by the binding energy of 284.8 eV for C 1s. Ultraviolet photoelectron spectroscopy (UPS, ESCALAB 250Xi, Thermo Fisher) measurements were carried out using a He I$\alpha$ photon source (21.22 eV). The current density – voltage (J–V) curves of fabricated devices were obtained from the forward and reverse scan with 10 mV intervals and 10 ms delay time under AM 1.5 G illumination (100 mW cm$^{-2}$) were collected using a source meter (Keysight B2901A) and a solar simulator (Enlitech SS-F5-3A). The EQE spectra was measured using an quantum efficiency measurement system (Enlitech QER-3011) in which the light intensity at every wavelength was calibrated with a Si detector before measurement. The maximum-power point (MPP) output was measured by testing the steady-state current density at the maximum-power-point voltage. Electrochemical impedance spectroscopy (EIS) was tested with the frequency range from 100 Hz to 1 MHz by the electrochemical workstation (Princeton Applied Research, P4000+) in the dark conditions at with a bias of 1 V. The amplitude is 10 mV.

Statistical Analysis: In order to facilitate comparison, part of the data is normalized, such as the time-resolved PL (TRPL) results (Figure 4b in the revised manuscript) and the stability results (Figure 5a-c and Figure S24 in the revised manuscript). The statistical results were obtained by presenting the photovoltaic parameters of different number of devices. The sample size, specific test, and data presentation of each statistical analysis was specified in the corresponding figure legend. The TRPL curves were fitted using OriginLab software. The scale bars of SEM, TEM and AFM images (Figure S17, Figure S18 and Figure S19 in the revised manuscript) were presented in the corresponding figure and specified in the figure legend. Specific details for all methods and softwares are discussed in the Characterization Section. Relevant content has been added in the revised manuscript on page 3.
Preparation and characterization of organic-inorganic (OI) complexes

General information

All syntheses were carried out under an inert atmosphere (nitrogen or argon) using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium/benzophenone (diethyl ether) or calcium hydride (dichloromethane) prior to use. The osmapentalyne 1 was synthesized according to the published literatures\(^1\). The other reagents and solvents were used as purchased from commercial sources without further purification. Column chromatography was performed on silica gel (200–300 mesh) in air. NMR spectra was collected on a Brucker AVANCE NEO 400 spectrometer (400 MHz) or Brucker AVANCE NEO 600 spectrometer (600 MHz). \(^1\)H and \(^{13}\)C\{}\(^1\)H\}\ NMR chemical shifts (δ) are relative to tetramethylsilane, and \(^{31}\)P\{}\(^1\)H\}\ NMR chemical shifts are relative to 85% H\(_3\)PO\(_4\). Two-dimensional and one-dimensional NMR spectra are abbreviated as HSQC (heteronuclear single quantum coherence), HMBC (heteronuclear multiple bond coherence) and DEPT (distortionless enhancement by polarization transfer). The absolute values of the coupling constants are given in hertz (Hz). Multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). The high-resolution mass spectra (HRMS) experiments were performed on a Thermo Scientific Q Exactive instrument.

Preparation and characterization of CL-CH\(_3\)

\[\begin{align*}
\text{HCOOC}[\text{Cl}]_6 & \quad \text{[Os]} = \text{Os(PPh}_3)_2 \\
\text{5} & \quad \text{4} \\
\text{3} & \quad \text{2} \\
\text{1} & \quad \text{BF}_4 \\
\text{Cs}_2\text{CO}_3, \text{CH}_2\text{Cl}_2, \text{RT, 1 d} & \quad \text{Yield = 78\%}
\end{align*}\]

A mixture of compound 1 (120 mg, 0.10 mmol), 4-methylphenol (54 mg, 0.50 mmol) and Cs\(_2\)CO\(_3\) (163 mg, 0.50 mmol) in 10 mL dichloromethane was stirred at RT for 1 d to give a red solution, and then the solid suspension was removed by filtration. The volume of the filtrate was reduced under vacuum to approximately 2 mL, and then loaded on silica gel column eluted by dichloromethane/methanol (20/1). The red band was collected, and the solvent was evaporated to dryness under vacuum to give a red solid. Yield, 99 mg, 78%.

\(^1\)H NMR plus \(^{13}\)C\{}\(^1\)H\}\ HSQC (600.1 MHz, CD\(_2\)Cl\(_2\)): δ = 12.51 (d, \(J_{HH} = 13.3\) Hz 1H, H7), 8.88 (m, 1H, H3), 8.84 (s, 1H, H5), 3.51 (s, 3H, COOC\(_3\)H), 1.85 (s, 3H, PhCH\(_3\)), -3.01 (t, \(J_{PP} = 22.7\) Hz, \(J_{HH} = 13.2\) Hz,1H, OsH), 7.90–6.25 ppm (48H, other aromatic protons). \(^{31}\)P NMR (242.9 MHz, CD\(_2\)Cl\(_2\)): δ = 9.01 (s, CPPh\(_3\)), -0.25 ppm (s, OsPPh\(_3\)). \(^{13}\)C NMR plus DEPT-135, \(^1\)H–\(^{13}\)C HSQC and \(^1\)H–\(^{13}\)C HMBC (150.9 MHz, CD\(_2\)Cl\(_2\)): δ = 251.4 (m, C1), 202.7 (t, \(J_{PP} = 12.5\) Hz, C7), 194.9 (d, \(J_{PC} = 27.2\) Hz, C4), 167.8 (d, \(J_{PC} = 15.5\) Hz, C3), 163.7 (s, COOCH\(_3\)), 157.9 (s, C5), 157.1 (s, C6), 136.5 (t, \(J_{PC} = 9.0\) Hz, C8), 123.0 (d, \(J_{PC} = 73.8\) Hz, C2), 50.8 (s, COOCH\(_3\)), 20.3 (s, PhCH\(_3\)), 166.9–111.1 ppm (other aromatic carbons). HRMS (ESI): \(m/z\) calcd for [C\(_{70}\)H\(_{58}\)O\(_3\)OsP\(_3\)]\(^+\), 1231.3208; found, 1231.3209.
Figure S1. The $^1$H NMR (600.1 MHz, CD$_2$Cl$_2$) spectrum of complex CL-CH$_3$.

Figure S2. The $^{31}$P{$^1$H} NMR (242.9 MHz, CD$_2$Cl$_2$) spectrum of complex CL-CH$_3$.
Figure S3. The $^{13}$C{^1}H NMR (150.9 MHz, CD$_2$Cl$_2$) spectrum of complex CL-CH$_3$.

Figure S4. Positive-ion ESI-MS spectrum of [CL-CH$_3$]$^+$ measured in methanol.

Preparation and characterization of CL-CF$_3$
A mixture of compound 1 (120 mg, 0.10 mmol), 4-trifluoromethylphenol (81 mg, 0.50 mmol) and Cs$_2$CO$_3$ (163 mg, 0.50 mmol) in 10 mL dichloromethane was stirred at RT for 1 d to give a red solution, and then the solid suspension was removed by filtration. The volume of the filtrate was reduced under vacuum to approximately 2 mL, and then loaded on silica gel column eluted by dichloromethane/methanol (20/1). The red band was collected, and the solvent was evaporated to dryness under vacuum to give a red solid. Yield, 95 mg, 72%.

$^1$H NMR plus $^1$H-$^{13}$C HSQC (600.1 MHz, CD$_2$Cl$_2$): δ = 12.70 (d, $J_{HH}$ = 13.3 Hz 1H, H7), 9.05 (m, 1H, H5), 8.98 (d, $J_{HH}$ = 4.7 Hz, 1H, H3), 3.55 (s, 3H, COOC$_3$H$_3$), 2.95 (td, $J_{PH}$ = 16.7 Hz, $J_{HH}$ = 13.5 Hz, 1H, OsH), 7.96–6.32 ppm (48H, other aromatic protons).

$^{31}$P NMR (242.9 MHz, CD$_2$Cl$_2$): δ = 9.05 (s, CPPh$_3$), 0.13 ppm (s, OsPPh$_3$).

$^{19}$F NMR (564.7 MHz, CD$_2$Cl$_2$): δ = -61.84 ppm (s, CF$_3$).

$^{13}$C NMR plus DEPT-135, $^1$H-$^{13}$C HMBC (150.9 MHz, CD$_2$Cl$_2$): δ = 251.0 (m, C1), 204.3 (t, $J_{PC}$ = 12.6 Hz, C7), 194.9 (d, $J_{PC}$ = 27.8 Hz, C4), 167.9 (d, $J_{PC}$ = 15.5 Hz, C3), 163.6 (s, COOCH$_3$), 159.4 (s, C5), 157.9 (s, C6), 138.7 (t, $J_{PC}$ = 9.0 Hz, C8), 123.5 (d, $J_{PC}$ = 73.6 Hz, C2), 51.0 (s, COOCH$_3$), 170.3–110.9 ppm (other aromatic carbons). HRMS (ESI): m/z calcd for [C$_{70}$H$_{55}$F$_3$O$_3$OsP$_3$]$^+$, 1285.2925; found, 1285.2921.

Figure S5. The $^1$H NMR (600.1 MHz, CD$_2$Cl$_2$) spectrum of complex CL-CF$_3$.  

H$_3$COOC

[Os] = Os(PPh$_3$)$_2$

CL-CF$_3$

F$_3$C

H$_3$COOC

[Os] = Os(PPh$_3$)$_2$

CL-CF$_3$

H$_3$COOC

[Os] = Os(PPh$_3$)$_2$

CL-CF$_3$
**Figure S6.** The $^{31}$P($^1$H) NMR (242.9 MHz, CD$_2$Cl$_2$) spectrum of complex CL-CF$_3$.  

**Figure S7.** The $^{13}$C($^1$H) NMR (150.9 MHz, CD$_2$Cl$_2$) spectrum of complex CL-CF$_3$. 
**Figure S8.** The $^{19}$F{¹H} NMR (564.7 MHz, CD$_2$Cl$_2$) spectrum of complex CL-CF$_3$.

**Figure S9.** Positive-ion ESI-MS spectrum of [CL-CF$_3$]$^+$ measured in methanol.

**X-ray Crystallographic Analysis**

The single crystals suitable for X-ray diffraction was grown from chloroform solution layered with
hexane. Single-Crystal X-ray diffraction data were collected on a Bruker SMART APEX2 area detector diffractometer with a Cu Kα radiation (λ = 1.54184 Å). Multi-scan absorption corrections was applied for CL-CH₃. Using Olex2[2], the structure of CL-CF₃ was solved with ShelXT[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using Least Squares minimization. All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model. The diffuse electron densities resulting from the residual solvent molecules in complex CL-CF₃ was removed from the data set by using the Solvent Mask routine of Olex2. CCDC-2160622 (CL-CF₃) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**Crystal Data for CL-CF₃:** C₇₀H₅₅ClF₃OsP₃ [C₇₀H₅₅F₃O₃OsP₃]Cl (Mr = 1319.70 g/mol): triclinic, crystal dimension 0.20 × 0.20 × 0.10 mm, space group P-1 (no. 2), a = 10.8099(5) Å, b = 12.8692(7) Å, c = 24.9865(11) Å, α = 88.596(2)°, β = 81.128(2)°, γ = 68.039(2)°, V = 3183.1(3) Å³, Z = 2, T = 100.0 K, μ(CuKα) = 5.316 mm⁻¹, Dcalc = 1.377 g/cm³, 57079 reflections measured (7.166° ≤ 2Θ ≤ 137.564°), 11620 unique (Rint = 0.0873, Rsigma = 0.0630) which were used in all calculations. The final R₁ was 0.0523 (I > 2σ(I)) and wR₂ was 0.1483 (all data). GOF = 1.115. Residual electron density (e. Å⁻³) max/min: 2.55/-1.71.

**Figure S10.** X-ray molecular structure for the cation of complex CL-CF₃ drawn with 50% probability level.

**Computational calculations**

All the calculations were performed with the Gaussian 09 software package.[5] The M06L/6-31G* level with SDD for Os atom.[6,7] The energies of their molecular orbitals were further calculated at the B3PW91/def2-TZVP level.[8,9]
Figure S11. Thermogravimetric measurements of CL-CH$_3$ and CL-CF$_3$ complexes.

Note: Thermogravimetric analyses (TGA) of CL-CH$_3$ and CL-CF$_3$ show that the initial decomposition temperatures (T5) as measured at the point of 5% weight loss are 217.1 °C and 207.6 °C, respectively.

Figure S12. Gaussian calculation summary of CL-CH$_3$ and CL-CF$_3$ complex.
Note: According to density functional theory (DFT), the dipole moments of CL-CF₃ and CL-CH₃ are 8.4 D and 11.04 D, respectively, due to the existence of strong electron-withdrawing Trifluoromethyl (-CF₃) group, CL-CF₃ exhibits higher dipole moment of than that of CL-CH₃ due to the existence of strong electron-withdrawing Trifluoromethyl (-CF₃) group.

**Figure S13.** FTIR spectra and fingerprint regions of pure PbI₂, CL-CH₃, CL-CF₃, PbI₂+CL-CH₃ and PbI₂+CL-CF₃ mixture in DMSO.

Note: The stretching vibration of C=O bond shifted from 1660 cm⁻¹ in pure CL-CH₃ and CL-CF₃ molecules to a lower wavenumber of 1643 cm⁻¹ for the PbI₂+CL-CH₃ and PbI₂+CL-CF₃ samples.
Figure S14. a) XPS survey spectra of control, CL-CH$_3$ and CL-CF$_3$ films. b-d) Os 4f core spectra, c) P 2p core spectra, and d) F 1s core spectra of control, CL-CH$_3$, CL-CF$_3$ films, respectively.

Note: It can be seen from the XPS survey spectra that control, CL-CH$_3$ and CL-CF$_3$ perovskite films all contain Pb, I, Cl, C, N, O. The appearance of Os 4f, P 2p and F 1s signal indicates the existence of OI complexes in the final film.
Figure S15. a) Pb 4f core spectra of perovskite films without and with CL-CH₃ and CL-CF₃ treatment. b) F 1s core spectra of PbI₂+CL-CF₃ and CL-CF₃ film.

Note: The Pb 4f peaks of control film are consistent with the reported binding energies of constituent elements of perovskite material, where Pb 4f⁵/₂ and Pb 4f⁷/₂ peaks are 143.1 and 138.2 eV, respectively. In the case of Pb 4f⁵/₂ and Pb 4f⁷/₂ of CL-CH₃ and CL-CF₃ treatment perovskite film, the peaks are 142.8, 137.97 eV and 142.7, 137.94 eV, respectively. The F 1s peaks of pure CL-CF₃ are 688.2eV. The F 1s peaks of PbI₂+ CL-CF₃ are 687.9eV.

Figure S16. XRD patterns of CL-CH₃, CL-CF₃ modified and control perovskite films.

Note: The XRD results suggest that the OI complexes will not affect the crystallinization.

Figure S17. STEM mappings of PSCs device cross-sectional images.

Note: The cross-sectional scanning transmission electronic microscopy (STEM) image of the device was presented, where all the functional layers are clearly observed, the thickness of the perovskite film, which is ≈500 nm.
Figure S18. Surface SEM images of control, CL-CH$_3$, CL-CF$_3$ films.
Note: The SEM results suggest that the O1 complexes will not affect the morphology.

Figure S19. AFM image of control, CL-CH$_3$, CL-CF$_3$ films.
Note: The O1 complexes treated films reveal smaller root mean square (RMS) values, which is helpful for charge extraction.

Figure S20. UV-Vis absorption spectra of control, CL-CH$_3$, CL-CF$_3$ films.
Figure S21. Tauc’s plot calculated from the UV-Vis absorption spectra with equation $(\alpha h \nu)^2 = A(h \nu - E_g)$, where $\alpha$ is the absorption coefficient, $h \nu$ is the photon energy, and $E_g$ is the bandgap.

Note: The UV–vis spectrum implies that the presence of CL-CH$_3$, CL-CF$_3$ molecules does not affect the bandgap of the perovskite materials. However, the existence of CL-CH$_3$, CL-CF$_3$ molecules makes the UV-Vis absorption intensity enhanced.

Figure S22. Ultraviolet photoelectron spectroscopy (UPS) of a) control, b) CL-CH$_3$ and c) CL-CF$_3$ films.

Note: Perovskite film the ionization energy (IE) according to equation $IE = 21.22 - [E_{cut-off} - E_{onset}]$. Combining with the optical bandgap derived from UV-vis absorption (Figure S19, Supporting Information), the position of conduction band minimum (CBM) and valence band maximum (VBM) of the films were ascertained, and the corresponding parameters are summarized in Table S1.
**Figure S23.** a) Dark J–V curves for the electron-only devices based on control, CL-CH₃ and CL-CF₃ films. b) Dark J–V curves for the hole-only devices based on control, CL-CH₃ and CL-CF₃ films.

Note: The typical dark J-V curves of electron-only devices with structure of ITO/SnO₂/Perovskite/PCBM/Ag. The typical dark J-V curves of hole-only devices with structure of ITO/NiOx/Perovskite/Spiro-OMeTAD/Au. According to $N_e = \frac{2V_{pp}L\varepsilon_0}{\varepsilon L^2}$, where $\varepsilon$ is the relative dielectric constant of perovskite, which is 62.23, $\varepsilon_0$ is the vacuum permittivity, $e$ is the elementary charge, and $L$ is the thickness of the perovskite film. It can be calculated that the electron-only devices trap-state density of control, CL-CH₃, and CL-CF₃ films are $2.37 \times 10^{16}$, $1.79 \times 10^{16}$, and $1.48 \times 10^{16}$ cm⁻³, respectively and the hole-only devices trap-state density of control, CL-CH₃, and CL-CF₃ films are $2.76 \times 10^{16}$, $2.41 \times 10^{16}$, and $2.14 \times 10^{16}$ cm⁻³, respectively. The electron mobility of the films was estimated using the Mott-Gurney equation as follows: $\mu = \frac{n_0 J D}{9 \varepsilon_0 e V^2}$, where $JD$ and $V$ are current density and voltage at the SCLC region. After carefully calculation, the hole mobility of control, CL-CH₃, and CL-CF₃ films located at $3.8 \times 10^{-2}$, $4.2 \times 10^{-2}$, and $5.7 \times 10^{-2}$ cm²V⁻¹S⁻¹, respectively. The results suggest that CL-CF₃ complex can effectively improve the hole mobility of the film.

**Figure S24** The operational stability of the corresponding unencapsulated devices under continuous 1 sun illumination in ambient environment.

**Note:** It is noted that after 32 hours illumination, the control device only retained 61% of its initial efficiency. In comparison, the CL-CH₃ device maintained 75% of its initial efficiency after 40 hours measurement. While, for the CL-CF₃ device, over 80% of its initial efficiency was maintained after 72 hours measurement.

**Table S1.** Conduction band minimum (CBM) and valence band maximum (VBM) of control, CL-CH₃ and CL-CF₃ films.
| Sample     | band gap [eV] | VBM [eV] | CBM [eV] |
|------------|--------------|----------|----------|
| Control    | 1.57         | 5.81     | 4.24     |
| CL-CH₃     | 1.57         | 5.75     | 4.18     |
| CL-CF₃     | 1.57         | 5.69     | 4.12     |

**Table S2.** TRPL parameters of the control, CL-CH₃ and CL-CF₃ films.

| Sample     | A₁   | τ₁ [ns] | A₂   | τ₂ [ns] | τₚₛₑ [ns] |
|------------|------|---------|------|---------|-----------|
| Control    | 0.34 | 91.10   | 0.68 | 377.40  | 346.6     |
| CL-CH₃     | 0.25 | 29.29   | 0.71 | 161.05  | 151.1     |
| CL-CF₃     | 0.45 | 24.43   | 0.60 | 126.39  | 113.5     |

Note: The fitting biexponential decay function was \( y = y_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right), \)

\[ \tau_{\text{pav}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}. \]

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