Supporting Information

In Situ Formation of an Inorganic Lead Oxysalt Surface Passivation Layer for Highly Efficient and Stable CsPbI$_3$ Perovskite Solar Cells

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Experimental sections

1. Precursor Solution Preparation

The CsPbI$_3$ perovskite precursor solutions were prepared by using the mole ratios of CsI: HPbI$_3$= 1:1 mol, 1 mol cesium iodide (CsI, 99%) and 1 mol Hydrogen Lead Iodine (HPbI$_3$, 99.99%) were dissolved with 0.75 mol lead source into 0.2 ml DMSO and 0.8ml DMF to yield 0.75 M precursor solutions. The CsPbI$_3$ precursor solutions were stirred at 60°C for 4-6 hours, and then filtered on 0.45μm micron filter. The above materials, CsI, HPbI$_3$, were purchased from Xi'an Polymer Light Technology. All the materials were used as received without further purification. The surface passivation layer was achieved by Ammonium Chromate (0.25, 0.5, 0.75, 1mg/ml) dissolved in IPA/MeOH (9:1) solution.

2. Device Fabrication

The FTO was cleaned with conductive glass cleaning agent, deionized water, and ethanol for 30min. The cleaned FTO substrate was then treated with UV ozone for 30 min. The compact TiO$_2$ (c-TiO$_2$) is made by immersing FTO in 200 ml cold water solution with 4.5 ml TiCl$_4$ for 1 hour at 70°C. After that, the substrate was annealed at

200°C for 30 minutes. Then the FTO/c-TiO$_2$ was treated with ultraviolet ozone again for 30 minutes. Then, 60 μl of CsPbI$_3$ perovskite precursor solution was drop cast onto FTO/c-TiO$_2$ preheated to 65°C. Next, the wet film is immediately rotated at a speed of 1000r/10s and 3000r/30s, and then annealed in the air at 210°C for about 10 minutes. For the HTL, a solution of 90 mg spiro-MeOTAD, 40μl of a prepared solution of 520 mg/mL lithium bis (trifluoromethylsulphonyl) imide, and 28.8 μl 4-tert-butylpyridine in 1 mL chlorobenzene was spun at 4000 rpm for 30 s. The devices were completed by depositing a 80 nm Au cathode by thermal evaporation under a pressure of 4×10^{-4} Pa.

3. Device Characterization

XRD patterns were obtained by using an X-ray diffractometer (SmartLab, Rigaku) with Cu Kα radiation (1.5418 Å). SEM images were taken with a SU8010 SEM (Hitachi). Absorption spectra were measured with a UV-2450 spectrophotometer (Shimadzu). The steady-state fluorescence and TRPL decay spectra were measured with a steady/transient state spectrophotometer (NanoLOG-TCSPC, USA) with an excitation wavelength of 450 nm. FTO with a sheet resistance of 15 Ω per square was obtained from Pilkington TEC. The active area of the solar cell was 0.09 cm^2. The $J-V$ curves were measured using a Keithley 2400 source meter together with a sunlight simulator (XES-300T1, SANEI Electric, AM 1.5 G), which was calibrated using a standard silicon reference cell (scan rate: 44 mV/s). The incident photon-to-electron conversion efficiency (IPCE) was measured in air using a QE-R measurement system (Enli Technology). Transient photovoltage decay measurements were performed using an electrochemical workstation (Zahner). X-ray photoelectron spectroscopy (XPS) was performed using an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation (hμ = 1486.6 eV). The contact angles were collected by using a Dataphysics OCA15EC. TOF-SIMS was performed using a TOF-SIMS5 (ION-TOF GmbH, Germany) by utilizing a cesium-ion beam (Sput. Rate=0.23 nm/s). The DLTS measurement was performed using a Phystech FT-1230 HERA-DLTS system. The device structure is FTO/TiO$_2$/perovskite/Spiro-OMeTAD/Ag. The samples were placed in a liquid-helium cryostat with a temperature scan range of 150-380 K at 2 K
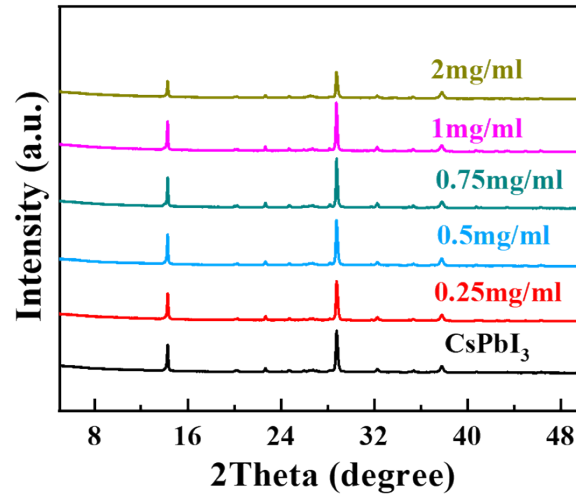
intervals.

Supporting Figures and Tables

Figure S1. XRD pattern of perovskite thin films with various concentration of AC passivation.
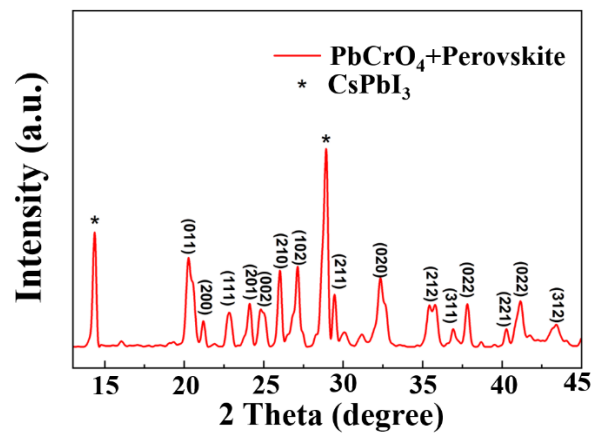
Figure S2. XRD patterns of films treated with AC precursor solution for 60 min, followed by 10 min annealing at 100 ℃.
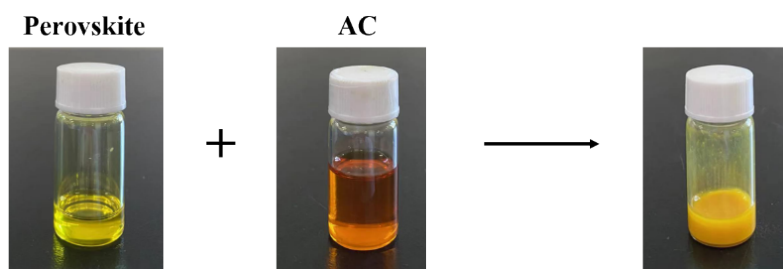
Figure S3. After adding AC to the perovskite precursors, the changing phenomenon of solution over time.
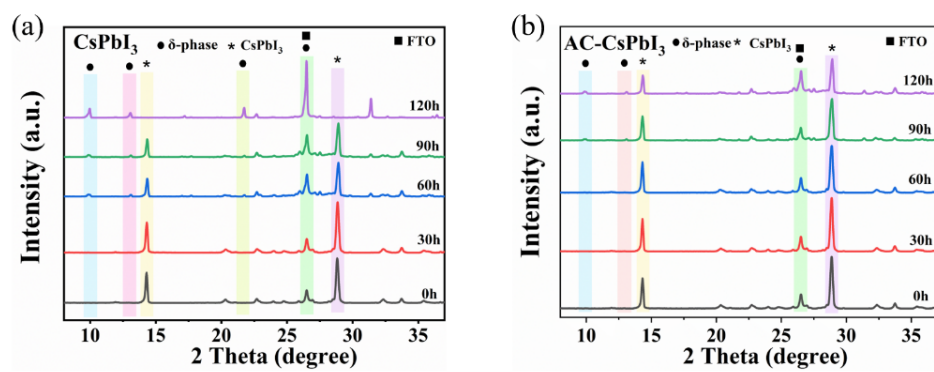
Figure S4. XRD patterns of CsPbI$_3$ film and AC-CsPbI$_3$ film exposed under the humidity condition for different times.
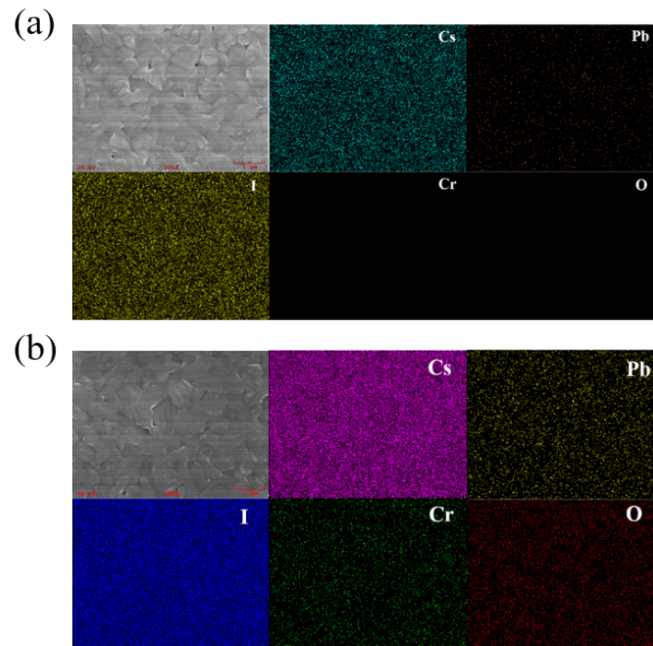
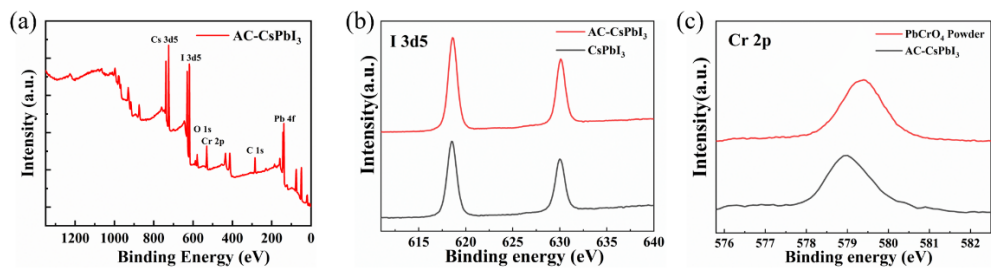**Figure S5.** The distribution of elements from inorganic perovskite thin film with and without AC treatment obtained from EDS characterization.

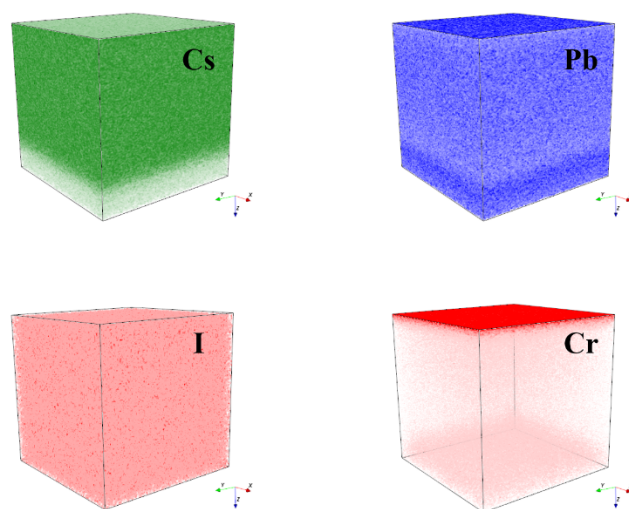**Figure S6.** (a) XPS spectra of the AC-CsPbI$_3$ perovskite film. Core-level (b) I 3d5 and (c) Cr 2p XPS spectra of the AC-CsPbI$_3$ perovskite.

Figure S7. Three-dimensional images of Cs, Pb, I, Cr in AC-CsPbI$_3$ perovskite film as obtained from the TOF-SIMS analysis.
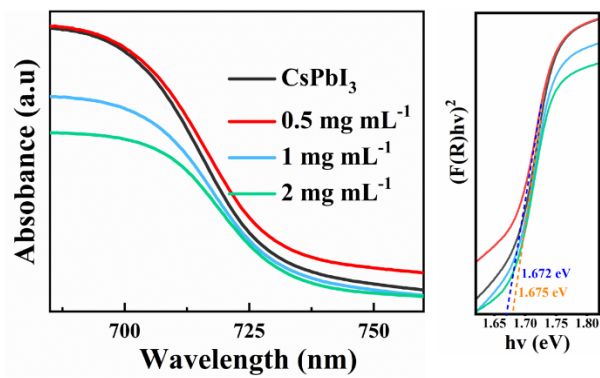
Figure S8. UV-vis spectra of the perovskite films prepared using different AC concentrations, and the corresponding Tauc plots.
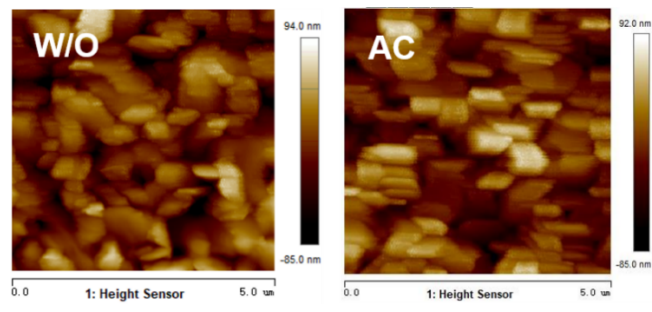
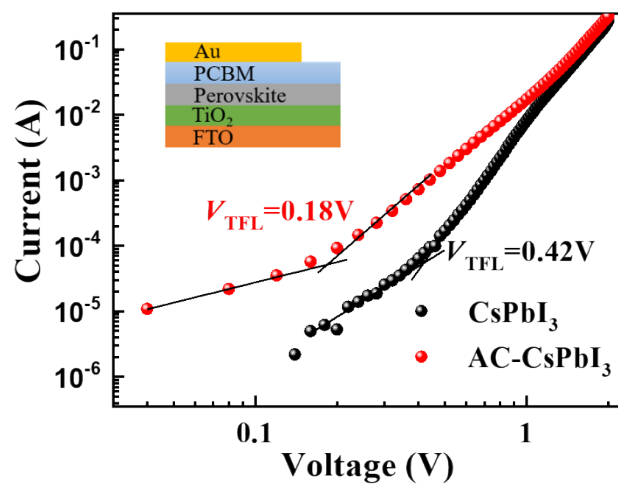**Figure S9.** AFM images of control and AC-treated perovskite films.

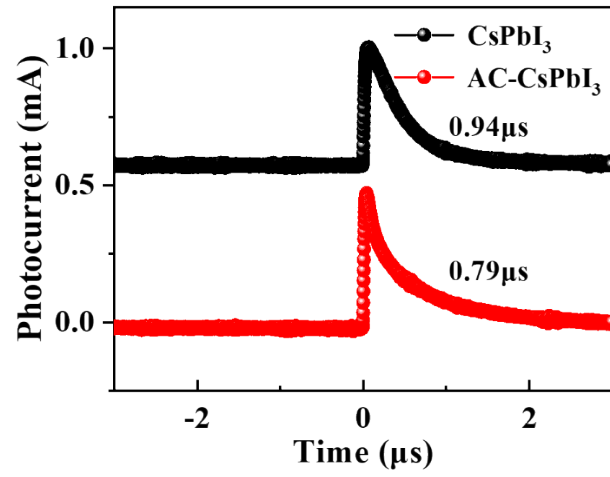**Figure S10.** Dark current–voltage responses of electron-only device (shown in the insets) with or without AC.

Figure S11. TPC decay curves of the photovoltaic devices surface layers with and without AC treatment.
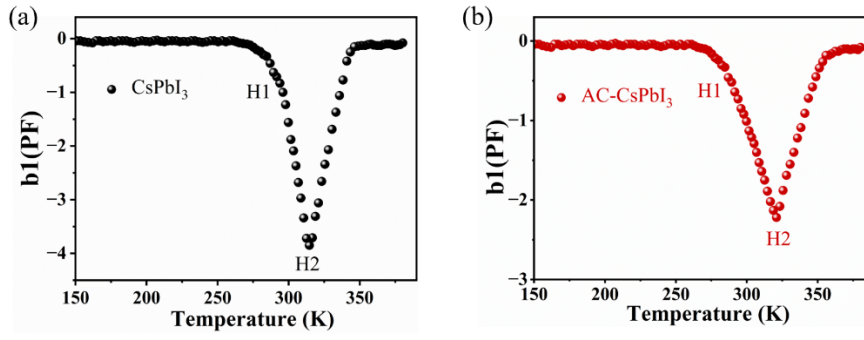
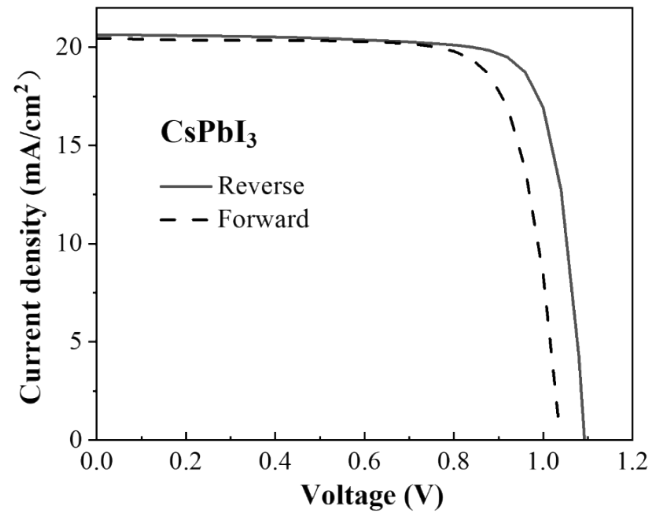**Figure S12.** The deep-level transient spectroscopy of (a) CsPbI$_3$ and (b) AC-CsPbI$_3$ samples.

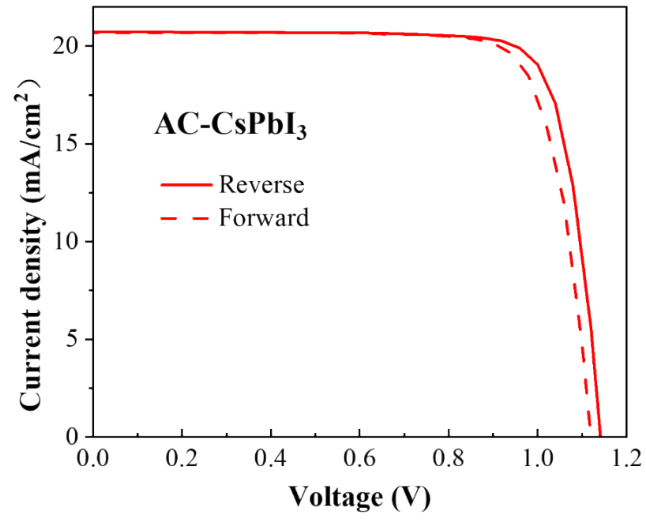**Figure S13.** Reverse and forward scan of CsPbI$_3$ PSCs.

Figure S14. Reverse and forward scan of AC-CsPbI$_3$ PSCs.
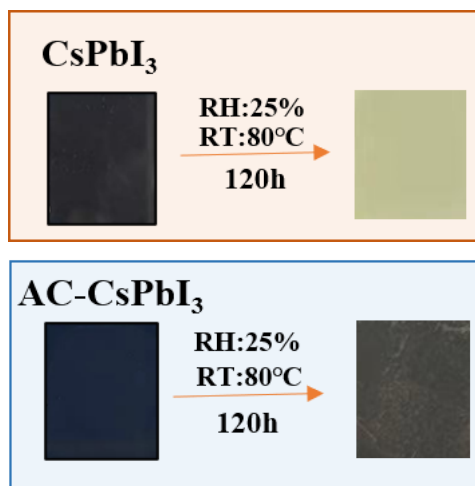
Figure S15. Photographs of CsPbI$_3$ and AC-CsPbI$_3$ films aged under the conditions of relative humidity of 25% and temperature of 80 °C.
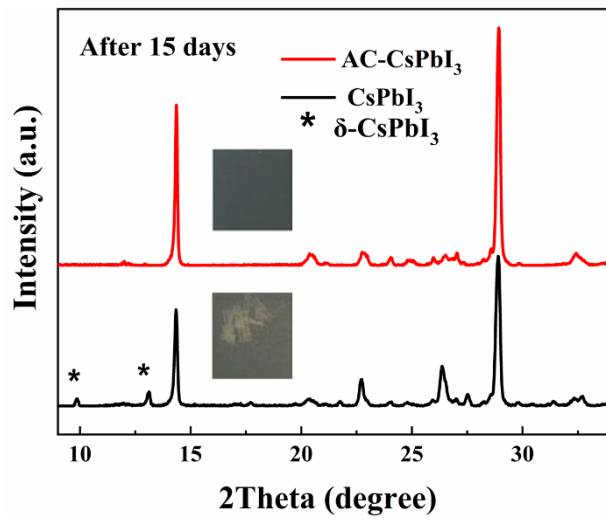
Figure S16. XRD patterns of the CsPbI$_3$ and AC-CsPbI$_3$ films after aging in air for 15 days.

Table S1. Time constants in TRPL obtained by bi-exponential fittings measured for the pristine and AC modified perovskite films based on glass substrate

Modification layer	τ_1(ns)	A_1(%)	τ_2(ns)	A_2(%)	τ_{ave}(ns)
CsPbI$_3$	5.39	46.29	24.26	53.71	20.94
AC-CsPbI$_3$	11.25	29.89	82.49	70.11	78.58

The average decay time (τ) was calculatedaccording to the formula:

$\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

Table S2. The measured electron trap-state density (nt, e) of perovskite with or without AC modification.

Modification layer	V_{TFL} (V)	nt, h (cm^{-3})
CsPbI$_3$	0.42	3.34×10^{15}
AC-CsPbI$_3$	0.18	1.43×10^{15}

Table S3. The measured hole trap-state density (nt, h) of perovskite film with or without AC modification.

Modification layer	V_{TFL} (V)	nt, h (cm^{-3})
CsPbI$_3$	0.54	4.29×10^{15}
AC-CsPbI$_3$	0.18	1.43×10^{15}

The trap density can be calculated from the following relation:
$$V_{TFL} = en_t L^2 / 2\varepsilon\varepsilon_0$$
where L is the thickness of the perovskite films, ε is the relative dielectric constant of the perovskite, and ε_0 is the vacuum permittivity.

Table S4. Parameters employed for the fitting of the impedance spectra of the devices based on the pristine and AC modified devices.

Electrolyde	Rs (Ω)	$Rrec$ (Ω)	$Crec$ (F)
CsPbI$_3$	19	14512	1.632E^{-8}
AC-CsPbI$_3$	15.67	36448	1.053E^{-8}

Table S5. The deep-level defect parameters (trap energy level (ET), capture cross section (σ), and trap density (NT)) from the DLTS spectra.

Sample	Trap	$E_T\text{-}E_V$ [eV]	σ [cm^2]	N_T [cm^{-3}]	Possible origin
CsPbI$_3$	H1	0.559	5.68×10^{-15}	7.42×10^{15}	I$_{Pb}$
	H2	0.482	3.13×10^{-15}	3.71×10^{15}	I$_{Cs}$
AC-CsPbI$_3$	H1	0.566	7.35×10^{-15}	4.82×10^{14}	I$_{Pb}$
	H2	0.485	2.31×10^{-15}	6.83×10^{14}	I$_{Cs}$

Table S6. Photovoltaic parameters for PSCs based on AC concentrations

AC-CsPbI$_3$	Jsc [mA/cm^2]	Voc [V]	FF [%]	PCE [%]
0mg/ml	20.24	1.08	80.70	17.78
0.25mg/ml	20.58	1.12	80.12	18.53
0.50mg/ml	20.69	1.13	80.79	19.04
0.75mg/ml	20.77	1.11	79.18	18.36

Table S7. Photovoltaic parameters for PSCs based on reaction time

Time	J_{sc} [mA/cm²]	V_{oc} [V]	FF [%]	PCE [%]
0s	20.51	1.08	79.65	17.93
10s	20.36	1.12	80.16	18.59
20s	20.72	1.14	80.33	19.08
30s	20.43	1.11	79.65	18.45

Table S8. Photovoltaic parameters of PSC

		J_{sc} [mA/cm²]	V_{oc} [V]	FF [%]	PCE [%]
CsPbI$_3$	R	20.46	1.09	79.98	17.96
	F	20.36	1.03	76.98	16.36
AC-CsPbI$_3$	R	20.69	1.14	80.76	19.09
	F	20.69	1.11	79.65	18.45