Supplementary Information (SI) for ChemComm.

Fluorescent Hole-Selective Contact for Ultraviolet-Stable Inverted Perovskite Solar Cells

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Experimental section

Materials

Cesium iodide (CsI), formamidinium iodide (FAI, 99.99%), lead iodide (PbI_2, 99.999%), lead bromide ($PbBr_2$, 99.999%), magnesium sulfate ($MgSO_4$, 99%), methylammonium bromide (MABr, 99.5%) and phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$, 99.9%) were sourced from Advanced Electionic Technology. Bathocuproine (BCP, 96%) was purchased from Alfa Aesar. The solvents, including N,N-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.9%), chlorobenzene (CB, spectrophotometric grade, 99.9%), isopropanol (IPA, 99.5%), ethyl acetate (EA, 99.9%) and petroleum ether (PE, 99.9%),were all purchased from Sigma-Aldrich. Diethyl ether (DEE, analytical pure) and potassium carbonate (K_2CO, analytical pure) were purchased from Sinopharm Chemical Reagent Co., Ltd. Lauryl amine (LA, 98%), trifluoroacetic acid (TFA, 99%) and dichloromethane (DCM, 99%) were purchased from Beijing InnoChem Science & Technology Co., Ltd. Methyl glycine hydrochloride (98%), ethyl acetylimine hydrochloride (95%) and aromatic aldehyde (98%) were all purchased from Bide Pharmatech Ltd. All chemicals and solvents described above were used as received without further purification.

Synthesis of methyl (Z)-2-((1-ethoxyethylidene)amino)acetate

A suspension of methyl glycine hydrochloride (15 g, 140 mmol) was prepared in a mixture of DEE (300 mL) and deionized water (48 mL). K_2CO (16.5 g, 140 mmol) was then added into the solution, and the resulting mixture was stirred at room temperature for 10 minutes. Subsequently, ethyl acetylimine hydrochloride (14.7 g, 140 mmol) was added, and the reaction was stirred for an additional 10 minutes. The organic layer was isolated using a separatory funnel, and the aqueous phase was extracted with a fresh portion of DEE (150 mL) under stirring for 10 minutes. The combined organic layers were dried over anhydrous $MgSO_4$, followed by solvent evaporation under reduced pressure to yield the crude product (10.35 g, 55%). This material was directly employed in subsequent synthetic steps without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ 4.08 (q, J = 7.1 Hz, 2H), 4.03 (s, 2H), 3.71 (s, 3H), 1.86 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101MHz, $CDCl_3$): δ (ppm): 171.20, 164.38, 60.46,51.29,50.60, 14.65,13.73. MS calcd. for $[M+H]^+$: 160.09, found: 160.10.

General procedure for synthesis of aromatic Schiff base 1

Syntheses of Schiff base was carried out by combining the selected aromatic aldehyde (10 mmol) with amine (11 mmol). The reaction was stirred at room temperature for 12 h. The solvent was removed in vacuum to obtain pure product, which was used for further reaction without purification.

Synthesis of FLUO-C_5-COOH

The aromatic Schiff base **1** (3.6 g, 10 mmol) was mixed with (Z)-2-((1-ethoxyethylidene)amino) acetate (1.7 g, 11 mmol) in anhydrous ethanol (20 mL) and stirred at room temperature for 12 hours. After completion, the solvent was evaporated under reduced pressure to yield the crude product, which was added to the solution of TFA and CH_2Cl_2 (V/V= 1/1, 10 mL) in 0°C for 2 hours. After completion, the solvent was evaporated under reduced pressure which was further purified via silica gel column chromatography using a mixture of EA and PE to obtain the desired **FLUO-C_5-COOH** (2.0 g, 58 %).^1H NMR (400 MHz, DMSO-d_6) δ 8.55 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 7.7 Hz, 1H), 7.25 (s, 1H), 7.13 (d, J = 8.1 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 6.77 (s, 1H), 3.54 (t, *J* = 7.5 Hz, 2H), 2.71 (s, 6H), 2.37 (s, 3H), 1.36 (s, 8H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.85, 170.59, 163.79, 155.10, 138.10, 133.14, 131.20, 127.21, 122.58, 122.03, 118.94, 45.54, 33.96, 28.81, 26.21, 24.53, 15.82, 14.55.

MS calculated for $[M+H]^+$: 344.19, measured:344.14.

Solution preparation

The NiO_x solution was prepared by mixing NiO_x nanocrystals (synthesized using our group's previous method) with deionized water at a concentration of 10 mg/mL. Ethanol solutions of FLUO-C_5-COOH and MeO-4PACz were prepared at a certain concentration, and the modified SAMs solution was obtained after mixing and stirring according to the molar ratio of 0.25% of FLUO-C_5-COOH and MeO-4PACz. The perovskite precursor solution (1.4 M) was prepared by dissolving PbI_2, $PbBr_2$, FAI, MABr, and CsI in a blended solvent of DMF and DMSO (4:1 volume ratio), following the stoichiometric formula $Cs_{0.05}(FA_{0.95}MA_{0.05})_{0.95}PbI_{0.95}Br_{0.05}$. A 30 mg/mL $PC_{61}BM$ solution was formulated by dissolving the material in chlorobenzene. For the BCP solution, 0.5 mg of BCP was mixed with 1 mL isopropyl alcohol. All solutions were filtered through a 0.22 μm filter prior to use.

Device fabrication

The FTO-coated glass substrates were ultrasonically cleaned sequentially in deionized (DI) water (with detergent solution), deionized water, acetone, isopropanol, and ethanol for 15 min each, followed by drying with a nitrogen gun. UV-Ozone treatment was then performed for 15 minutes. 45 μL of NiO_x solution was spin-coated onto the conductive glass substrate at 4000 rpm for 30 s. The coated substrate was then annealed at 150°C for 30 s, cooled to room temperature, and transferred into a N_2-filled glove box for subsequent operations. The modified SAMs film was prepared by spinning coating at 5000 rpm for 30 s and annealing 30 min at 150°C, and then the perovskite film was prepared by one-step method. The perovskite layer was obtained by taking 45 μL of perovskite precursor solution, pre-coating at 1000 rpm for 5 s, then spin coating at 5000 rpm for 20 s, extracting with 150 μL of CB anti-solvent at the final 3 s, followed by annealing at 100°C for 30 min. The PC$_{61}$BM electron transport layer was fabricated by spin-coating 30 μL of PC$_{61}$BM solution onto the pre-deposited perovskite light-absorbing layer at 3000 rpm for 30 s and annealing at 100°C for 10 min. Subsequently, a BCP/isopropanol (IPA) solution was spin-coated at 5000 rpm for 1 min and annealed at 70°C for 5 min. Finally, a 200 nm Ag electrode was evaporated using a 0.06 cm^2 mask in a thermal evaporator (PD400S, Wuhan PDVacuum).

Characterizations:

The current density-voltage (*J-V*) curves of perovskite solar cells were measured under AM 1.5 G illumination (100mW/cm^2) using a Newport 94023A solar simulator and a Keithley 2400 source. The external quantum efficiency (EQE) spectrum was recorded with a TLS130BMY-300X EQE system (Newport). Both *J-V* and EQE tests were conducted in ambient air without encapsulation, with the active area defined by a 0.06 cm^2 metal mask. Surface topography and roughness of the films were analyzed by atomic force microscopy (AFM, Bruker Multimode 8). Cross-sectional and surface images of perovskite layers were captured via scanning electron microscopy (SEM, Hitachi SU8010). Contact angles were measured using an OCA15 goniometer (Data Physics). X-ray diffraction (XRD) patterns were acquired on a Bruker D8 Advance diffractometer with Cu K_α radiation ($\lambda = 1.5406$ Å). UV-vis absorption spectra were collected using a Shimadzu UV-2600 spectrophotometer. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were conducted on Thermo Fisher ESCALAB 250XI (USA), with a □5 V bias applied during UPS measurements. Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) decay profiles were obtained using an Edinburgh Instruments FLS980 spectrometer. The rotary evaporator used in the synthesis process is model R210 and is manufactured by BUCHI in Switzerland, and the superconducting nuclear magnetic resonance spectrometer is the AVANXCE-400M, manufactured by Bruker, Germany.

Supplementary figures and tables

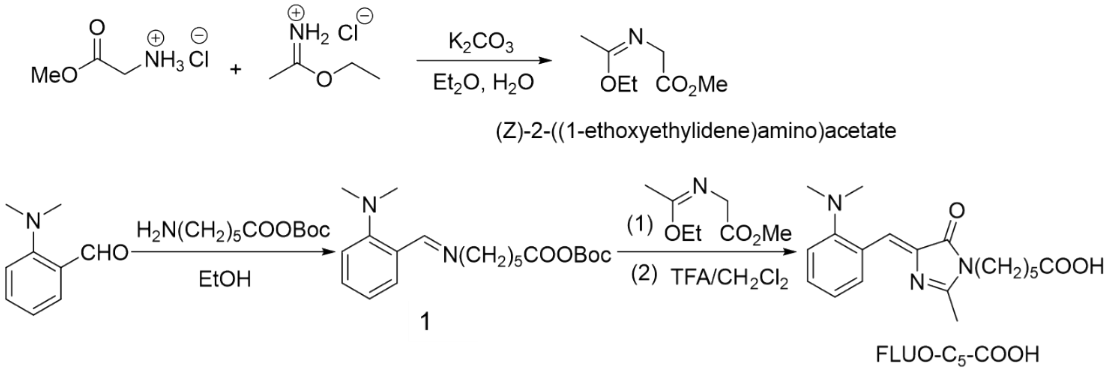

Fig. S1. Schematic diagram of the synthesis route of FLUO-C_5-COOH.

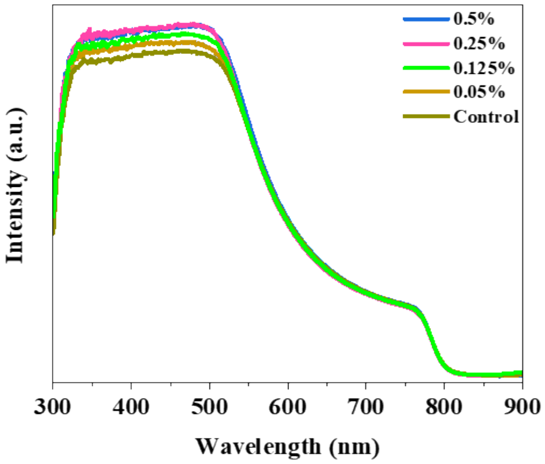

Fig. S2. The UV–vis absorption spectra of perovskite films treated with different concentrations of FLUO-C_5-COOH.

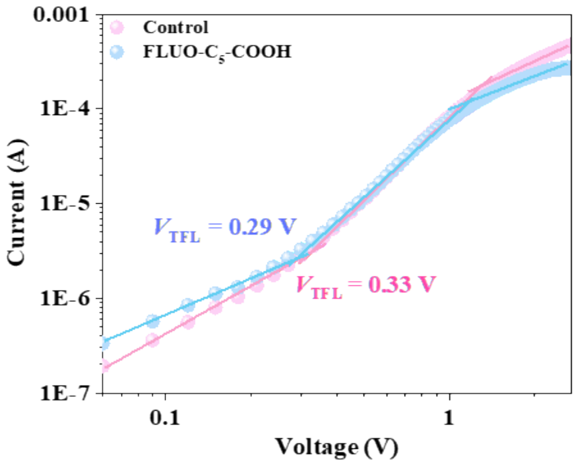

Fig. S3. The SCLC of hole-only devices with the structure of FTO/NiO_x/MeO-4PACz or MeO-4PACz:FLUO-C_5-COOH/Perovskite/Spiro-OMeTAD/Ag.

The trap density N_t was calculated using the trap-filled limit voltage model (Supplementary Reference 1):

$$N_t = \frac{2V_{TFL}\varepsilon\varepsilon_0}{eL^2} \# (1)$$

where V_{TFL} is the trap-filled limiting voltage (V), L = 550 nm (the thickness of perovskite film), e = 1.602×10^{-19} C (elementary charge), $\varepsilon_0 = 8.854\times10^{-12}$ F/m (vacuum permittivity), and $\varepsilon = 30$ (permittivity of perovskite).

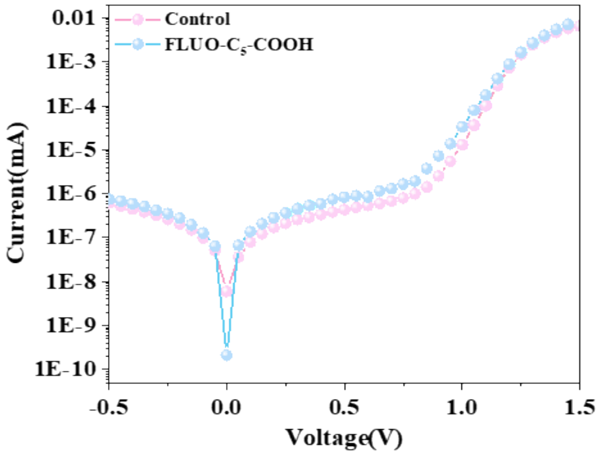

Fig. S4. Dark current of control and FLUO-C_5-COOH-modified devices.

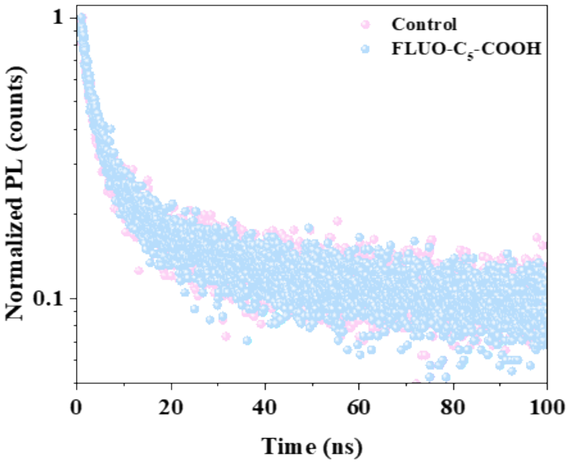

Fig. S5. TRPL spectra of FTO/NiO_x/MeO-4PACz/Perovskite and FTO/NiO_x/MeO-4PACz:FLUO-C_5-COOH/Perovskite films.

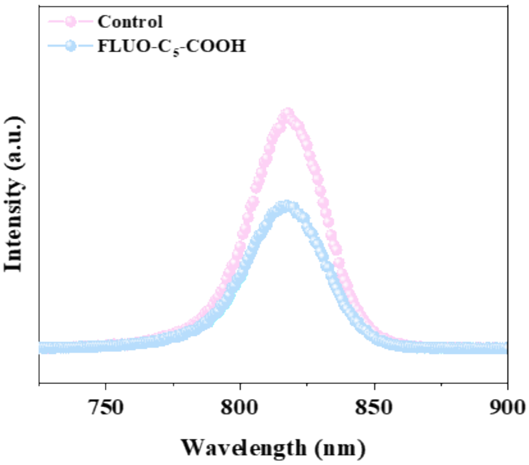

Fig. S6. PL spectra of FTO/NiO_x/MeO-4PACz/Perovskite and FTO/NiO_x/MeO-4PACz:FLUO-C_5-COOH/Perovskite films.

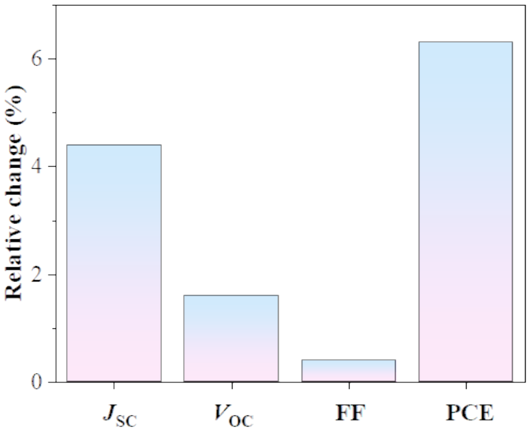

Fig. S7. Relative change plot of key parameters of control and modified devices.

Table S1 Summary of device performance for PSCs with different concentrations of FLUO-C_5-COOH treatment.

Device	V_{OC} (V)	J_{SC} (mA/cm^2)	PCE (%)	FF (%)
Control	1.17	22.63	20.24	76.5
0.5%FLUO-C_5-COOH	1.17	22.36	21.59	82.5
0.25%FLUO-C_5-COOH	1.17	23.55	22.53	81.8
0.125%FLUO-C_5-COOH	1.17	22.12	20.44	79.0
0.05%FLUO-C_5-COOH	1.17	21.23	20.37	82.0

Table S2 Parameters of TAS of perovskite based on bare NiO_x/MeO-4PACz and NiO_x/MeO-4PACz:FLUO-C_5-COOH substrates.

Device	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_{avg} (ns)
Control	3.49	0.90	109.7	0.11	87.81
FLUO-C_5-COOH	3.74	0.90	93.86	0.11	71.70

Table S3 Photovoltaic parameters for champion PSCs based on NiO_x/MeO-4PACz and NiO_x/MeO-4PACz:FLUO-C_5-COOH HTLs.

Device	V_{OC} (V)	J_{SC} (mA/cm^2)	PCE (%)	FF (%)
Control	1.152	22.55	21.19	81.5
FLUO-C_5-COOH	1.17	23.55	22.53	81.8

Table S4 Comparison table of key parameters of the control and modified devices.

Parameter	Control	FLUO-C_5-COOH	Absolute change（Δ）	Relative change（%）
J_{SC} (mA/cm^2)	22.55	23.55	+1.00	+4.4%
V_{OC} (V)	1.152	1.17	+0.018	+1.6%
FF (%)	81.5	81.8	+0.3	+0.4%
PCE (%)	21.19	22.53	+1.34	+6.3%

Supplementary References

1. W. Luo, H. Wen, Y. Guo, T. Yin, H. Tan, Z. Zhang, S. Si, Z. Zhang, H. Wu and S. Huang, *Adv. Funct. Mater.*, 2024, **34**, 2400474.