Supporting Information:

Non-toxic Solvent Processed Tin-Halide Perovskite Solar Cells via Weak Coordination

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Experimental section

Materials

N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), N,N-diethylformamide (DEF, 99%, Adamas-beta), dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich), chlorobenzene (CB, 99.8%, Sigma-Aldrich), isopropanol (IPA, 99.5%, Adamas-beta), formamidinium iodide (FAI, 99.9%, Great-Cell), methylammonium bromide (MABr, 99.9%, Great-Cell), tin (II) iodide (SnI_2, 99.99%, Adamas-beta), tin fluoride (SnF_2, 99%, Sigma-Aldrich), phenethylammonium iodide (PEAI, >99.5%, Xi'an Polymer Light Technology Corp.), tin powder (Sn, 99.8%, Sigma-Aldrich), poly (3,4-ethylene dioxythiophene)-poly (styrene sulfonate) (PEDOT:PSS, 4083, CleviousTM HTL Solar), bathocuproine (BCP, >98%, Adamas-beta), silver (Ag, 99.9%, Trillion Metals), indium tin oxide (ITO, 7-9 Ω sq^{-1}, Advanced Election Technology CO.Ltd). All the commercial materials were purchased and used directly without any other processing.

C_{60}-ETPA synthesis[1]: C_{60} (0.366g, 0.5mmol) and 2eq. of (2-ethylhexyl)glycine, 1 eq. of 4-(bis(4-methoxyphenyl)amino)benzaldehyde were dissolved in 60ml of 1,2-DCB. The mixture was heated for 2 h at 120℃ under nitrogen atmosphere with intense stirring. After cooled down and the solution was removed under pressure. The crude

product was purified through column chromatography (petroleum ether/ethyl acetate = 9/1 vol/vol) to obtain C_{60}-ETPA (0.108 g; yield: 29.5%) as a brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (s, 2H), 7.38 (s, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 6.99 (dd, *J* = 21.0, 8.2 Hz, 5H), 6.81 (d, *J* = 8.5 Hz, 4H), 5.08 (d, *J* = 9.3 Hz, 1H), 4.99 (s, 1H), 4.06 (d, *J* = 9.4 Hz, 1H), 3.80 (s, 6H), 3.10 (t, *J* = 11.5 Hz, 1H), 2.52 (t, *J* = 9.9 Hz, 1H), 2.05 – 1.98 (m, 2H), 1.46 (s, 9H), 1.36 (s, 4H), 1.31 (s, 6H), 1.26 (d, *J* = 15.3 Hz, 1H), 1.07 (q, *J* = 7.5 Hz, 2H), 1.00 (s, 5H), 0.92 (s, 1H), 0.10 (s, 17H). HR-MS: (ESI) m/z: C90H38N2O2; calculate: 1178.2766; found: 1178.2933.

Device preparation

First of all, ITO glass was carefully cleaned with detergent, deionized water, ethanol, acetone, and isopropyl for 20 min, sequentially. Then, the cleaned ITO substrates were blown dry with N_2 and exposed to UV light for 15 min. 100 μL PEDOT: PSS solution was spin-coated on the ITO substrate at 4000 rpm for 50 s followed with 30 min annealing at 140 ℃ under ambient conditions. For the perovskite precursor solution (1M) with a chemical composition of $FA_{0.75}MA_{0.25}SnI_{2.75}$ $Br_{0.25}$, 129.0 mg FAI, 28.0 mg MABr, 372.5 mg SnI_2 together with 5 mg Sn^0 and 16.7 mg SnF_2 were dissolved in DMF: DMSO (800 μL: 200 μL) or DEF: DMSO (600 μL: 400 μL), respectively. In addition, 12% PEAI was added and stirred for 1 h before spin-coating. After filtered with 0.22 μm PTFE filters, 45 μL precursor solution was spin-coated on the prepared substrate at 8000 rpm for 60 s. At 12 s after the start of spin-coating, 150 μL CB was dropped on the film. And then the film was annealed at 80 ℃ for 10 min. Next, 50 μL C_{60}-ETPA (20 mg ml^{-1} in CB) was coated on the film at 2000 rpm for 30 s followed by annealed at 70 ℃ for 10 min. Then 90 μL BCP (5 mg ml^{-1} in IPA) was spin-coated at 6000 rpm for 30 s and annealed at 70 ℃ for 10 min. Finally, the Ag electrode (100 nm) was evaporated at a speed of 2 A s^{-1} under a high vacuum level.

Characterization

X-ray diffraction (XRD) analysis was measured by a MiniFlex 600 (Rigaku) X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm, 40 kV, 100 mA). The Fourier

transform infrared (FTIR) spectra were detected by a Fourier transform infrared spectroscopy (Bruker). ^{13}C NMR spectra were obtained by Avance III HD (Bruker, 400MHz). The dynamic light scattering (DLS) spectra was measured by Malvern Zetasizer ZEN 3600. The atomic force microscope (AFM) was conducted by Alpha300 RA. The UV-vis absorption spectra and the diffuse reflection spectroscopy were probed by UV-2600 (Shimadzu). The steady photoluminescence (PL) and time-resolved photoluminescence (TRPL) were collected by PTI QuantaMaster 8000 (HORIBA). *J-V* characteristics were performed by solar simulator (San-EI Electric) under standard AM 1.5G (100 mW cm^{-2}) illumination in N_2 atmosphere. The external quantum efficiency (EQE) was measured by QE-R (Enlitech). The transient photocurrent (TPC), transient voltage (TPV), Mott-Schottky (M-S), and impedance spectroscopy (IS) were tested by Paios 4.0 system with a 60 mW LED light source (FLUXiM). The effective area of the device is 0.096 cm^2.

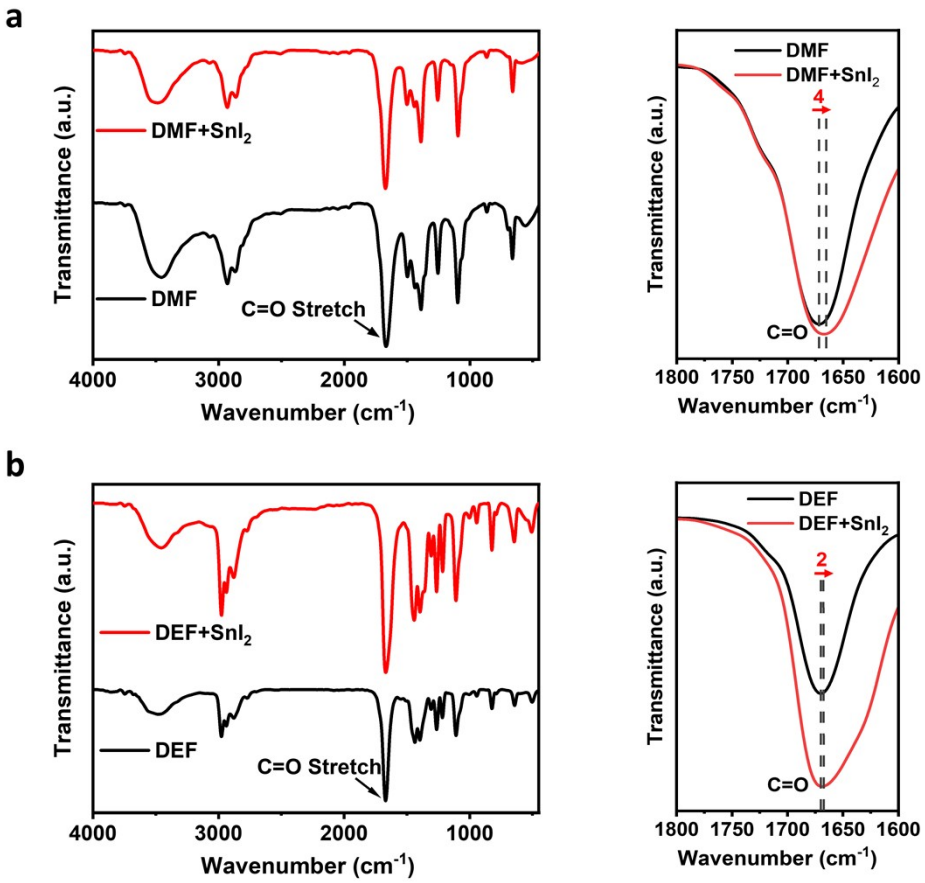

Fig. S1. The FTIR plots of SnI_2 solution dissolved in (a) DMF and (b) DEF, separately.

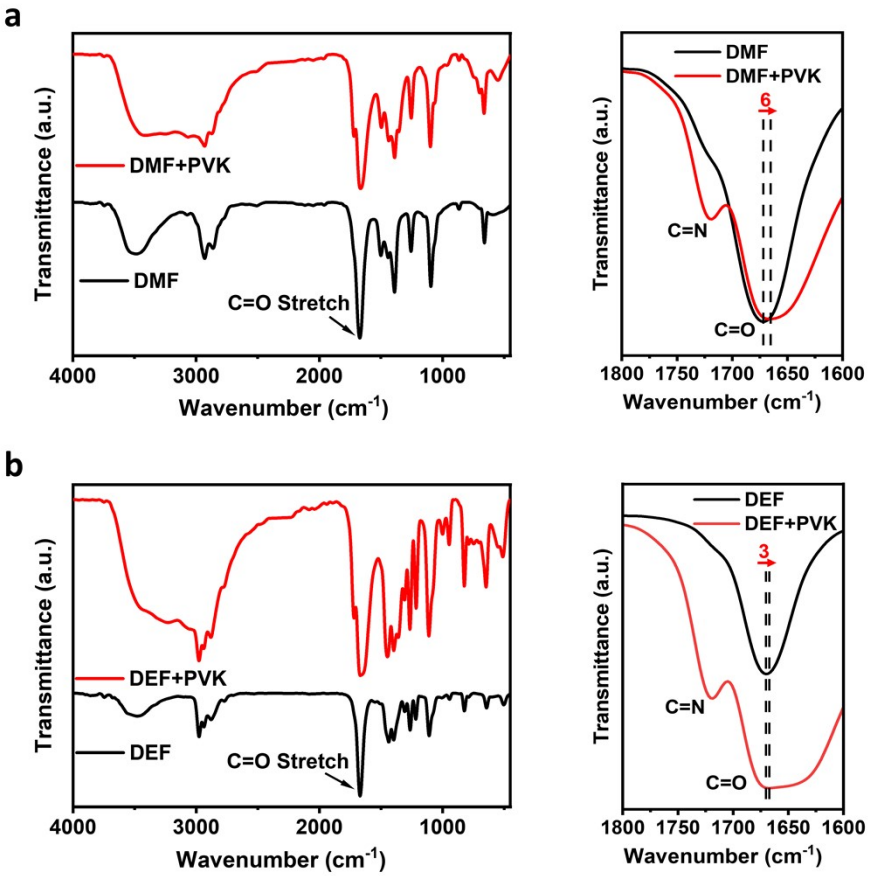

Fig. S2. The FTIR plots of perovskite solution dissolved in (a) DMF and (b) DEF, separately.

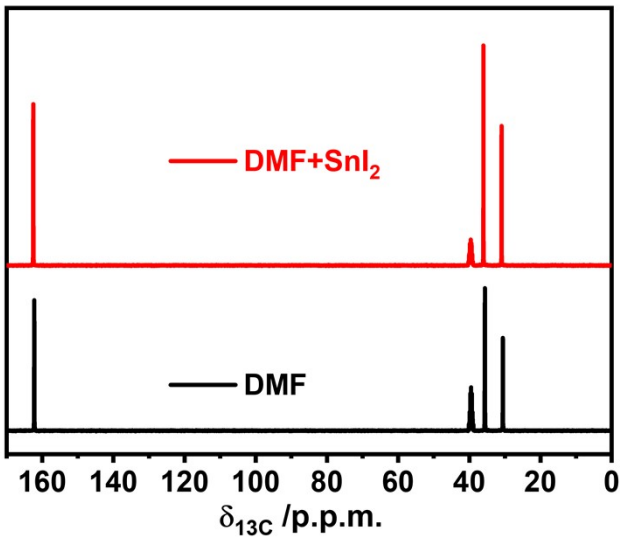

Fig. S3. The ^{13}C NMR full plot of SnI_2 solution dissolved in DMF.

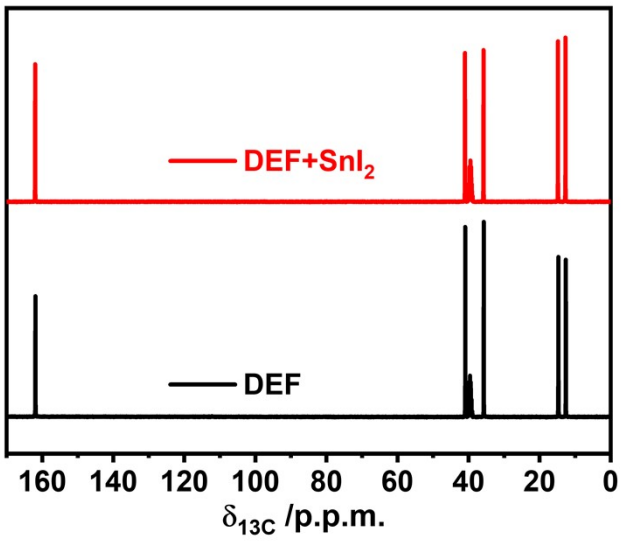

Fig. S4. The ^{13}C NMR full plot of SnI_2 solution dissolved in DEF.

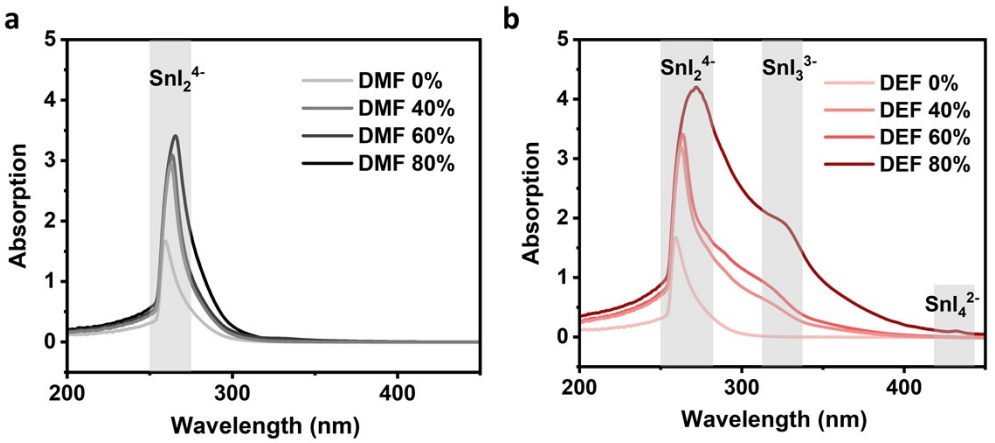

Fig. S5. Gradient test of the UV-vis absorption spectra of SnI_2 solution (0.5 mM) with different (a) DMF and (b) DEF ratios.

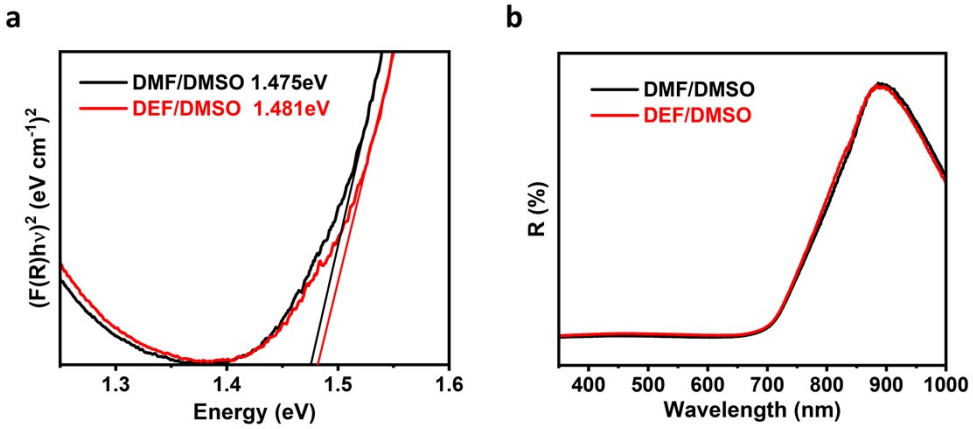

Fig. S6. The diffuse reflection spectroscopy curves of the DMF and DEF perovskite films.

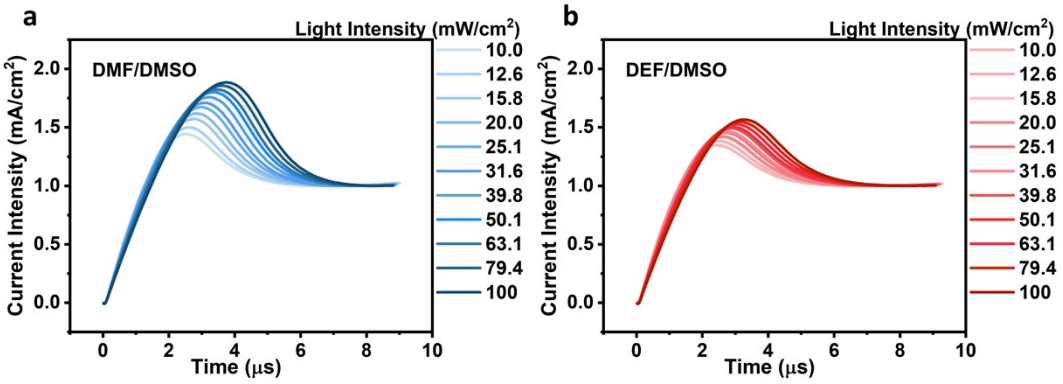

Fig. S7. Photo-CELIV plots of the (a) DMF and (b) DEF device.

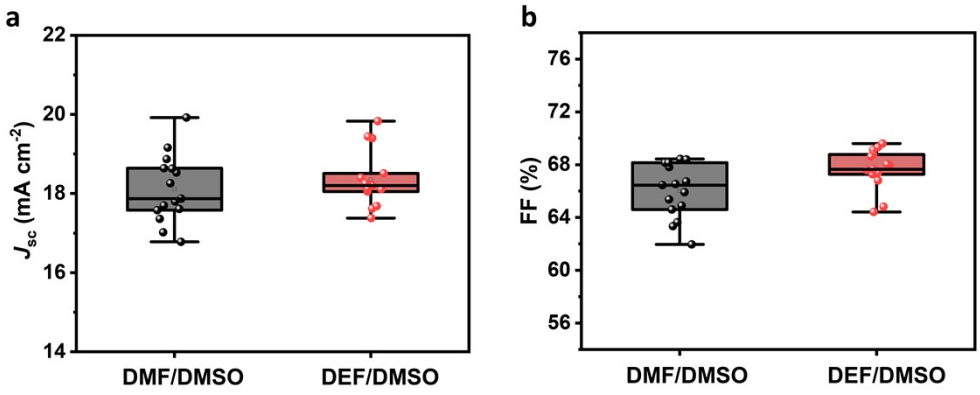

Fig. S8. The box diagram of (a) J_{sc} and (b) FF for 15 independent devices.

Table S1. The acute toxicity of solvents.[2]

mg/kg	DMF	DMPU	DMI	DEF	DMSO
mouse intraperitoneal (LD_{50})	650	1300	2840	3200	N/A
rat intraperitoneal (LD_{50})	400	N/A	N/A	1740	8200

Table S2. The safety, health, and environmental scoring of solvents.[3]

Solvent	Safety Score	Health Score	Environment Score	Ranking
DMF	3	9	5	Hazardous
DMSO	1	1	5	Recommended
DMI	1	6	7	Problematic
DEF	3	2	5	Recommended
DMPU	1	6	7	Problematic

Table S3. Some physical property parameters of DMF, DEF and DMSO.

Solvent	Boiling Point (℃)	Dielectric Constant	Viscosity (cP)	Vapor Pressure (mmHg)
DMF	153	36.7	0.92	3.87
DEF	177	28.4	1.14	1.21
DMSO	189	46.7	1.99	0.61

Table S4. The fitted PL lifetime from TRPL spectra of control and target perovskite films.

	A_1(%)	τ_1(ns)	A_2(%)	τ_2(ns)	τ_{avg}(ns)
DMF	40.4	13.3	59.6	5.2	10.3
DEF	33.0	18.8	67.0	7.9	13.8

Table S5. Detailed photovoltaic performance parameters of control and target device.

	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
DMF	760	18.6	67.8	9.61
	(767 ± 9.47)	(18.1 ± 0.84)	(66.0 ± 2.03)	(9.17 ± 0.28)
DEF	805	18.3	68.6	10.08
	(796 ± 11.9)	(18.4 ± 0.68)	(67.7 ± 1.48)	(9.88 ± 0.29)

Table S6. Detailed information of EQE measurement compared with *J-V* parameters.

	J_{sc} (mA/cm^2)	J_{int} (mA/cm^2)
DMF	18.6	18.7
DEF	18.3	18.1

Reference

1. C. Wu, W. Zhu, S. Wang, Z. Cao, L. Ding and F. Hao, *Chem. Commun.*, 2022, 58, 13007-13010.
2. Acute toxicity from hazardous substances data bank https://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm.
3. D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada and P. J. Dunn, *Green Chem.*, 2016, **18**, 288-296.