Supplementary Material

Organic-inorganic hybrid quasi-2D perovskites incorporated with fluorinated additives for efficient and stable four-terminal tandem solar cells

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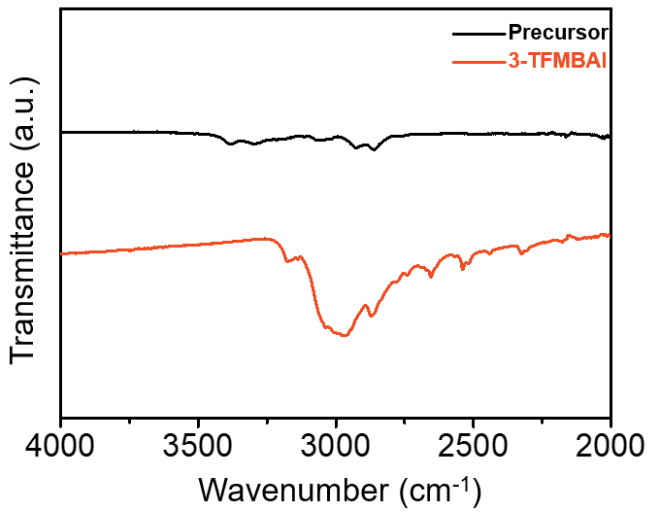
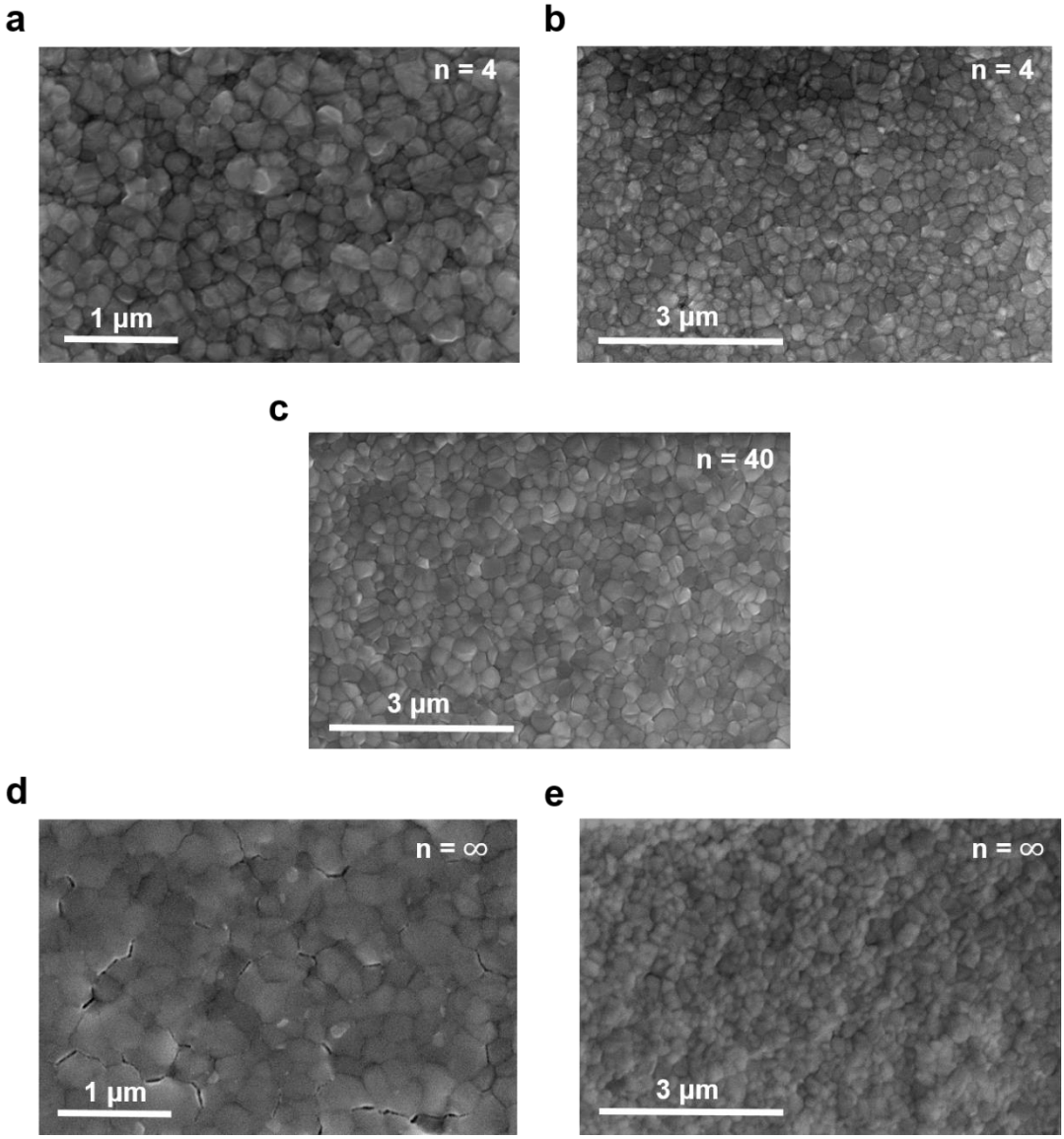
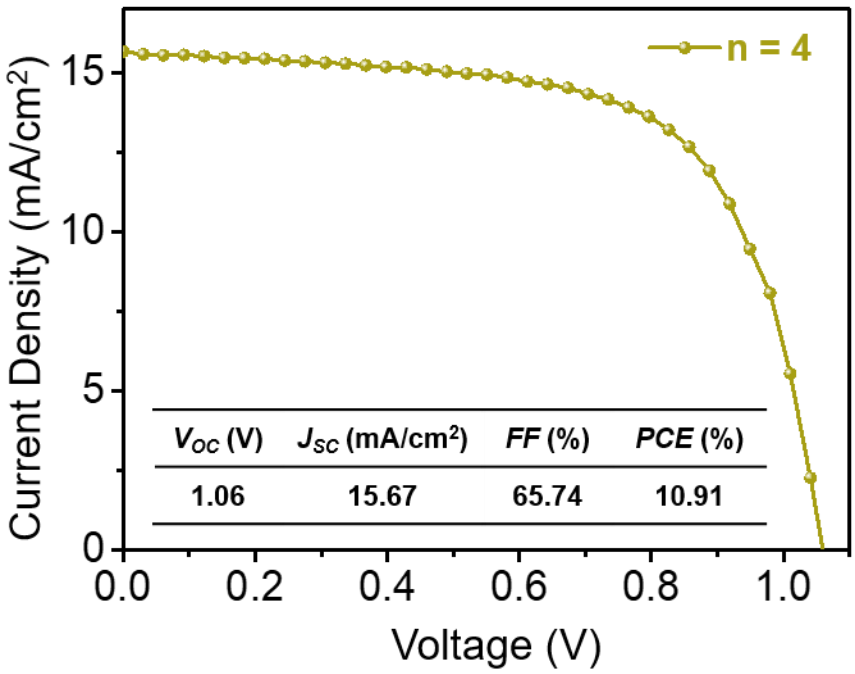
Supplementary Figure 1. Optical image of the as-synthesized 3-TFMBAI powder.



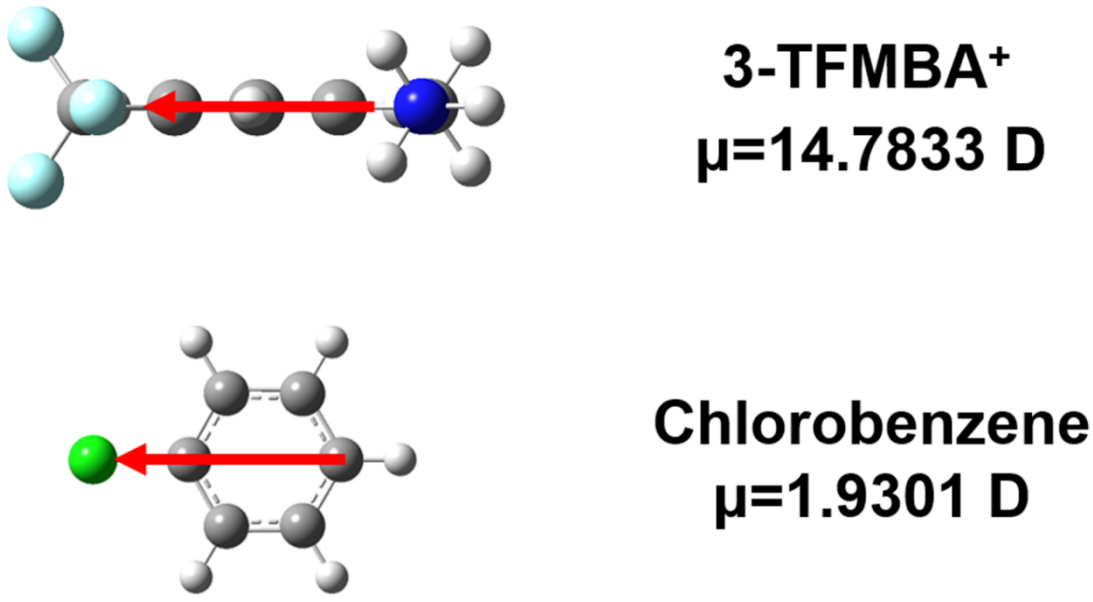
Supplementary Figure 2. Fourier transform infrared (FTIR) spectra of the 3-(trifluoromethyl)benzylamine precursor and as-synthesized 3-TFMBAI.



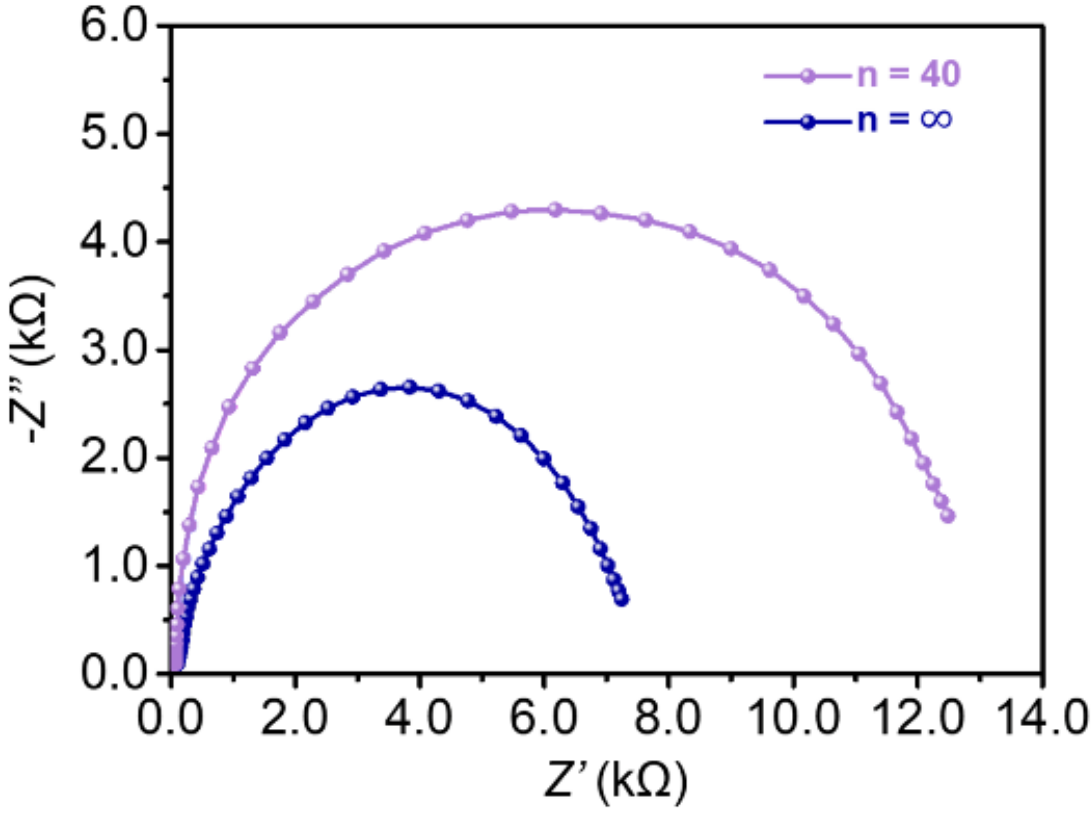
Supplementary Figure 3. Top-view SEM images of the surface morphologies of the $(3\text{-TFMBA})_2(Cs_{0.17}FA_{0.83})_{n-1}Pb_n(I_{0.83}Br_{0.17})_{3n-1}I_2$ perovskite films with (a, b) n = 4, (c) n = 40 and (d, e) n = ∞.



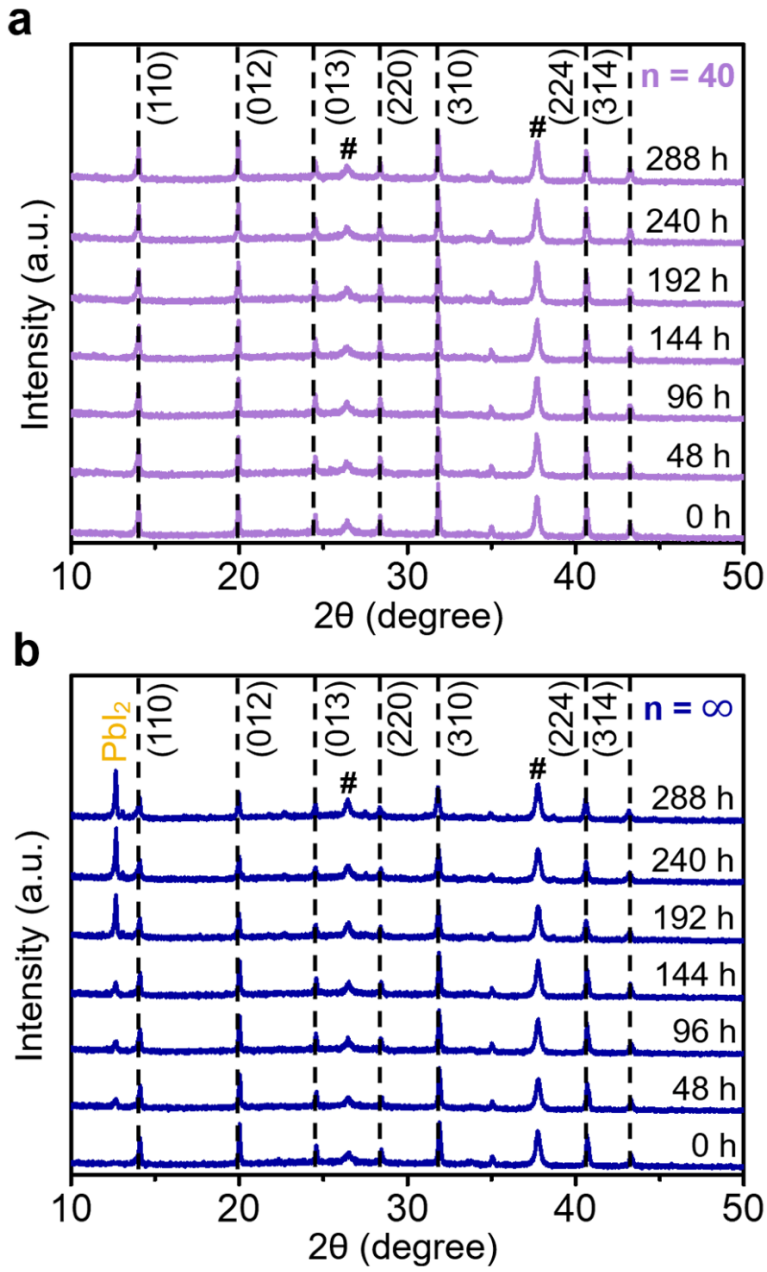
Supplementary Figure 4. Typical *J-V* plot and corresponding photovoltaic parameters of the $(3\text{-TFMBA})_2(Cs_{0.17}FA_{0.83})_{n-1}Pb_n(I_{0.83}Br_{0.17})_{3n-1}I_2$ perovskite solar cell with n = 4 measured at a scan rate of 200 mV/s.



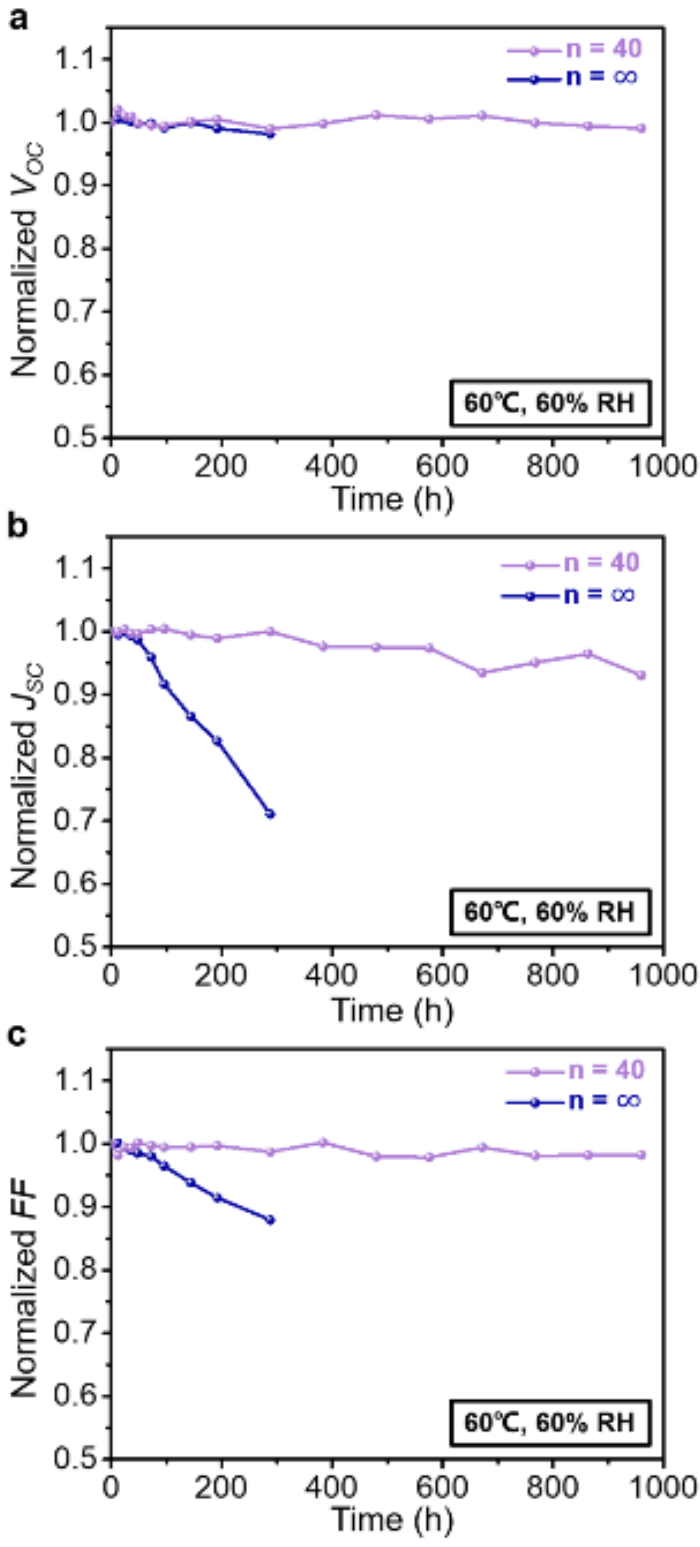
Supplementary Figure 5. Gaussian calculation on the dipole moments of 3-TFMBA^+ cation and chlorobenzene.



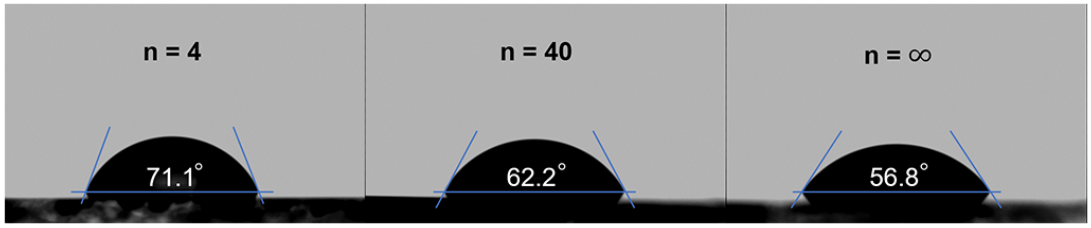
Supplementary Figure 6. Electrochemical impedance spectroscopy (EIS) results of PSCs with n = 40 and n = ∞.



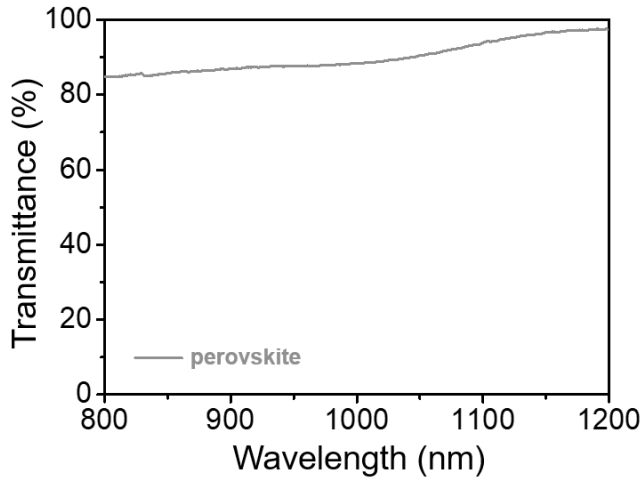
Supplementary Figure 7. XRD patterns of the perovskite films with (a) n = 40 and (b) n = ∞ without encapsulation under continuous heating at 60 °C and simultaneous exposure to humid air with a RH of 60%.



Supplementary Figure 8. Normalized (a) *Voc*, (b) *Jsc and* (c) *FF* retentions of different PSCs without encapsulation under continuous heating at 60 ℃ and simultaneous exposure to humid air with a RH of 60%.



Supplementary Figure 9. Contact angle images of deionized water droplets on (3-TFMBA)$_2$(Cs$_{0.17}$FA$_{0.83}$)$_{n-1}$Pb$_n$(I$_{0.83}$Br$_{0.17}$)$_{3n-1}$I$_2$ perovskite films with different n values (n = 4, 40 and ∞).



Supplementary Figure 10. Light transmittance of (3-TFMBA)$_2$(Cs$_{0.17}$FA$_{0.83}$)$_{n-1}$Pb$_n$(I$_{0.83}$Br$_{0.17}$)$_{3n-1}$I$_2$ perovskite layer with n = 40 in near infrared region. The average transmittance in near infrared region was measured to be ~90%.

Supplementary Table 1. XPS binding energies of different elements measured from the $(3\text{-TFMBA})_2(Cs_{0.17}FA_{0.83})_{n-1}Pb_n(I_{0.83}Br_{0.17})_{3n-1}I_2$ perovskite films with different n values.

Binding energy (eV)	Br $3d_{5/2}$	Br $3d_{3/2}$	I $3d_{5/2}$	I $3d_{3/2}$	Pb $4f_{7/2}$	Pb $4f_{5/2}$	Cs $3d_{5/2}$	Cs $3d_{3/2}$	F 1s
n = 1	68.2	69.2	619.3	630.8	137.0	141.9	--	--	686.1
n = 4	68.4	69.3	619.2	630.7	136.9	141.8	724.8	738.7	686.0
n = 40	68.5	69.4	619.2	630.7	136.9	141.8	724.8	738.8	686.0
n = ∞	68.6	69.4	619.2	630.7	136.9	141.8	724.9	738.8	--

Supplementary Table 2. Br 3d, I 3d, Pb 4f, Cs 3d and F 1s XPS peak area, relative sensitivity factor (RSF), corrected RSF, atomic concentration and atomic concentration ratio of $(3\text{-TFMBA})_2(Cs_{0.17}FA_{0.83})_{n-1}Pb_n(I_{0.83}Br_{0.17})_{3n-1}I_2$ perovskite films with different n values, respectively.

Br 3d	Peak area	RSF	Corrected RSF	Atomic concentration	Atomic concentration ratio (versus n = 1)
n = 1	772.8	1.149	68.653	11.26	1.000
n = 4	993.6	1.149	68.653	14.47	1.286
n = 40	1124.8	1.149	68.653	16.38	1.455
n = ∞	1132.6	1.149	68.653	16.50	1.466
I 3d	**Peak area**	**RSF**	**Corrected RSF**	**Atomic concentration**	**Atomic concentration ratio (versus n = 1)**
n = 1	46336.5	6.302	385.766	120.1	1.000
n = 4	35394.3	6.302	385.766	91.75	0.764
n = 40	31335.7	6.302	385.766	81.23	0.676
n = ∞	30932.4	6.302	385.766	80.18	0.668
Pb 4f	**Peak area**	**RSF**	**Corrected RSF**	**Atomic concentration**	**Atomic concentration ratio (versus n = 1)**
n = 1	18295.6	9.000	546.489	33.48	1.000

n = 4	17940.8	9.000	546.489	32.83	0.981
n = 40	17592.4	9.000	546.489	32.19	0.962
n = ∞	17666.2	9.000	546.489	32.33	0.966
Cs 3d	**Peak area**	**RSF**	**Corrected RSF**	**Atomic concentration**	**Atomic concentration ratio (versus n = 4)**
n = 1	--	11.80	729.535	--	--
n = 4	2984.4	11.80	729.535	4.091	1.000
n = 40	3850.8	11.80	729.535	5.278	1.290
n = ∞	4104.8	11.80	729.535	5.627	1.375
F 1s	**Peak area**	**RSF**	**Corrected RSF**	**Atomic concentration**	**Atomic concentration ratio (versus n = 1)**
n = 1	48033.9	4.430	268.236	179.1	1.000
n = 4	13318.3	4.430	268.236	49.65	0.277
n = 40	1242.9	4.430	268.236	4.634	0.026
n = ∞	--	4.430	268.236	--	--

Supplementary Table 3. The fitting parameters A_1, A_2, τ_1, τ_2 and τ_{avg} of the time-resolved PL curves measured from the (3-TFMBA)$_2$($Cs_{0.17}FA_{0.83}$)$_{n-1}$$Pb_n$($I_{0.83}Br_{0.17}$)$_{3n-1}$$I_2$ perovskite films with different n values.

Parameters	**n = 4**	**n = 40**	**n = ∞**
A_1	0.294	0.465	0.500
A_2	0.706	0.535	0.500
τ_1	78.90	13.02	18.78
τ_2	17.02	158.15	155.16
τ_{avg}	35.24	90.65	86.97

Supplementary Table 4. Photovoltaic parameters of 24 individual (3-TFMBA)$_2$($Cs_{0.17}FA_{0.83}$)$_{n-1}Pb_n$($I_{0.83}Br_{0.17}$)$_{3n-1}I_2$ PSCs based on 80 nm-thick Au counter electrodes with n = 40 or n = ∞, respectively.

n = 40	***Jsc*** **(mA/cm^2)**	***Voc*** **(V)**	***FF***	***PCE*** **(%)**	**n = ∞**	***Jsc*** **(mA/cm^2)**	***Voc*** **(V)**	***FF***	***PCE*** **(%)**
1	21.57	1.22	78.54	20.68	**1**	22.09	1.17	77.14	20.03
2	21.56	1.22	78.42	20.59	**2**	22.09	1.17	76.50	19.72
3	21.57	1.22	77.92	20.46	**3**	22.03	1.16	76.86	19.71
4	21.52	1.22	77.18	20.27	**4**	21.99	1.16	76.33	19.39
5	21.88	1.21	77.27	20.49	**5**	21.80	1.17	75.92	19.44
6	21.15	1.21	77.12	19.76	**6**	21.97	1.15	75.57	19.04
7	21.45	1.20	77.02	19.85	**7**	21.52	1.16	74.74	18.60
8	21.08	1.20	78.58	19.91	**8**	21.88	1.13	76.36	18.87
9	21.44	1.21	76.57	19.83	**9**	22.13	1.17	71.74	18.58
10	21.11	1.22	75.45	19.37	**10**	21.24	1.16	75.55	18.56
11	21.30	1.20	75.47	19.29	**11**	21.20	1.16	75.52	18.63
12	21.26	1.20	75.52	19.27	**12**	21.01	1.16	76.05	18.52
13	21.00	1.20	76.58	19.36	**13**	21.58	1.14	72.99	18.02
14	21.35	1.15	77.42	19.08	**14**	21.25	1.14	76.08	18.49
15	20.75	1.21	74.03	18.52	**15**	20.97	1.16	74.95	18.28
16	20.89	1.19	75.52	18.77	**16**	20.90	1.14	77.54	18.43
17	20.49	1.21	76.07	18.84	**17**	20.97	1.15	75.64	18.29
18	20.54	1.21	76.28	18.95	**18**	20.92	1.15	74.08	17.87
19	20.39	1.20	74.09	18.12	**19**	20.09	1.13	76.92	17.50
20	20.13	1.20	74.40	18.04	**20**	20.51	1.14	76.40	17.93
21	20.21	1.21	75.64	18.46	**21**	20.00	1.13	77.82	17.66
22	20.61	1.19	71.35	17.50	**22**	20.56	1.11	76.01	17.38
23	19.57	1.19	76.02	17.66	**23**	20.93	1.12	74.65	17.46

24	19.56	1.17	75.52	17.33	**24**	21.11	1.09	71.82	16.56

Supplementary Table 5. Photovoltaic performances of champion PSCs based on 80 nm-thick Au counter electrodes and different n values (10, 20, 40, and 60) under 100 mW/cm^2 AM 1.5G illumination.

	V_{OC} (V)	J_{SC} (mA/cm^2)	*FF* (%)	*PCE* (%)
n = 10	1.09	17.29	66.49	12.57
n = 20	1.14	19.98	72.36	16.48
n = 40	1.22	21.79	78.54	20.89
n = 60	1.19	21.98	75.42	19.72

Supplementary Table 6. The average transmittance in near infrared region and the internal resistance of the whole PSCs with different thickness of Au counter electrode.

Au thickness (nm)	Average Transmittance (%)	Resistance (Ω)
10	32.46	5.63×10^5
20	20.58	83.9
30	18.10	76.9
40	12.86	68.6

Supplementary Table 7. Photovoltaic performances of champion PSC with n = 40 and 20 nm-thick Au counter electrode and champion tandem solar cell based on silicon solar cell covered by PSC under 100 mW/cm^2 AM 1.5G illumination.

	V_{OC} (V)	J_{SC} (mA/cm^2)	*FF* (%)	*PCE* (%)
Perovskite (top)	1.19	20.98	76.59	19.11
Silicon (bottom)	0.51	12.91	67.70	4.42
Tandem	--	--	--	23.53

Supplementary Table 8. Photovoltaic parameters of 48 individual (3-TFMBA)$_2$($Cs_{0.17}FA_{0.83}$)$_{n-1}Pb_n$($I_{0.83}Br_{0.17}$)$_{3n-1}I_2$ perovskite solar cells with n = 40 based on 20 nm-thick Au counter electrodes.

n = 40	***Jsc*** **(mA/cm^2)**	***Voc*** **(V)**	***FF***	***PCE*** **(%)**	**n = 40**	***Jsc*** **(mA/cm^2)**	***Voc*** **(V)**	***FF***	***PCE*** **(%)**
1	20.92	1.19	76.52	19.05	**25**	19.96	1.18	76.23	17.96
2	20.99	1.19	76.58	19.11	**26**	20.47	1.15	75.31	17.79
3	20.94	1.19	76.48	19.03	**27**	20.14	1.16	73.64	17.21
4	20.80	1.18	75.82	18.61	**28**	19.87	1.16	73.58	17.01
5	20.73	1.18	76.88	18.85	**29**	19.79	1.19	72.55	17.04
6	20.86	1.18	75.76	18.63	**30**	19.87	1.15	75.03	17.19
7	20.56	1.18	76.46	18.54	**31**	19.80	1.18	73.13	17.04
8	20.88	1.18	75.64	18.60	**32**	19.81	1.18	74.03	17.23
9	20.50	1.17	75.10	18.08	**33**	19.54	1.18	74.69	17.23
10	20.86	1.18	74.95	18.41	**34**	19.63	1.18	74.16	17.13
11	20.94	1.16	74.19	18.07	**35**	19.82	1.17	74.97	17.42
12	20.89	1.13	76.79	18.09	**36**	18.98	1.17	76.40	16.95
13	20.53	1.18	75.67	18.33	**37**	19.40	1.15	74.51	16.62
14	20.72	1.16	76.08	18.36	**38**	18.90	1.16	76.50	16.82
15	20.68	1.17	74.97	18.17	**39**	19.04	1.15	76.36	16.70
16	20.41	1.18	76.12	18.34	**40**	19.82	1.13	75.29	16.79
17	20.77	1.12	75.31	17.58	**41**	18.98	1.15	75.89	16.62
18	21.02	1.15	72.77	17.59	**42**	19.40	1.14	76.13	16.86
19	20.13	1.18	73.45	17.51	**43**	18.45	1.15	76.24	16.11
20	20.10	1.18	73.99	17.50	**44**	19.04	1.14	74.52	16.11
21	19.91	1.18	75.22	17.68	**45**	19.82	1.14	72.92	16.41
22	20.17	1.17	74.78	17.71	**46**	18.98	1.13	75.94	16.34
23	20.31	1.16	76.32	17.98	**47**	20.01	1.13	69.08	15.65
24	19.90	1.19	75.91	17.90	**48**	20.00	1.14	69.24	15.78

Supplementary Table 9. Photovoltaic parameters of 48 individual (3-TFMBA)$_2$($Cs_{0.17}FA_{0.83}$)$_{n-1}$$Pb_n$($I_{0.83}Br_{0.17}$)$_{3n-1}$$I_2$ perovskite solar cells with n = ∞ based on 20 nm-thick Au counter electrodes.

n = 40	***Jsc*** **(mA/cm^2)**	***Voc*** **(V)**	***FF***	***PCE*** **(%)**	**n = 40**	***Jsc*** **(mA/cm^2)**	***Voc*** **(V)**	***FF***	***PCE*** **(%)**
1	21.47	1.15	74.07	18.32	**25**	20.51	1.14	72.30	16.92
2	21.54	1.15	73.71	18.25	**26**	21.03	1.11	68.47	16.03
3	21.49	1.15	71.79	17.72	**27**	20.70	1.12	69.89	16.22
4	21.36	1.14	73.17	17.83	**28**	20.43	1.12	71.62	16.43
5	21.29	1.14	72.86	17.72	**29**	20.36	1.15	68.78	16.06
6	21.42	1.14	72.70	17.74	**30**	20.43	1.11	70.55	16.04
7	21.32	1.14	73.95	17.96	**31**	20.36	1.14	70.67	16.36
8	21.44	1.14	71.68	17.48	**32**	20.36	1.13	71.35	16.48
9	21.06	1.13	72.60	17.34	**33**	20.10	1.14	70.01	16.04
10	21.42	1.14	70.70	17.22	**34**	20.19	1.14	69.90	16.03
11	21.49	1.12	70.78	17.08	**35**	20.38	1.13	68.13	15.72
12	21.45	1.09	73.60	17.17	**36**	19.54	1.13	70.41	15.53
13	21.08	1.14	72.51	17.43	**37**	19.96	1.11	71.93	15.93
14	21.28	1.13	71.33	17.08	**38**	19.46	1.12	72.64	15.88
15	21.24	1.13	70.90	17.05	**39**	19.60	1.11	72.85	15.83
16	20.97	1.14	70.86	16.95	**40**	20.37	1.09	71.78	15.88
17	21.33	1.08	72.23	16.70	**41**	19.54	1.11	71.65	15.59
18	21.58	1.11	69.00	16.53	**42**	19.96	1.10	71.00	15.60
19	20.69	1.14	70.87	16.77	**43**	19.01	1.11	72.18	15.17
20	20.66	1.14	72.02	16.91	**44**	19.60	1.10	71.83	15.42
21	20.47	1.14	71.99	16.80	**45**	20.38	1.10	67.51	15.08
22	20.72	1.13	71.37	16.78	**46**	19.54	1.09	70.53	15.07
23	20.86	1.12	70.72	16.52	**47**	20.57	1.09	65.95	14.81
24	20.45	1.14	72.31	16.93	**48**	20.56	1.10	64.96	14.69