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Supporting Information

Effect of bidentate and tridentate additives on photovoltaic performance and stability of perovskite solar cells

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Figures S1-12

Tables S1-5

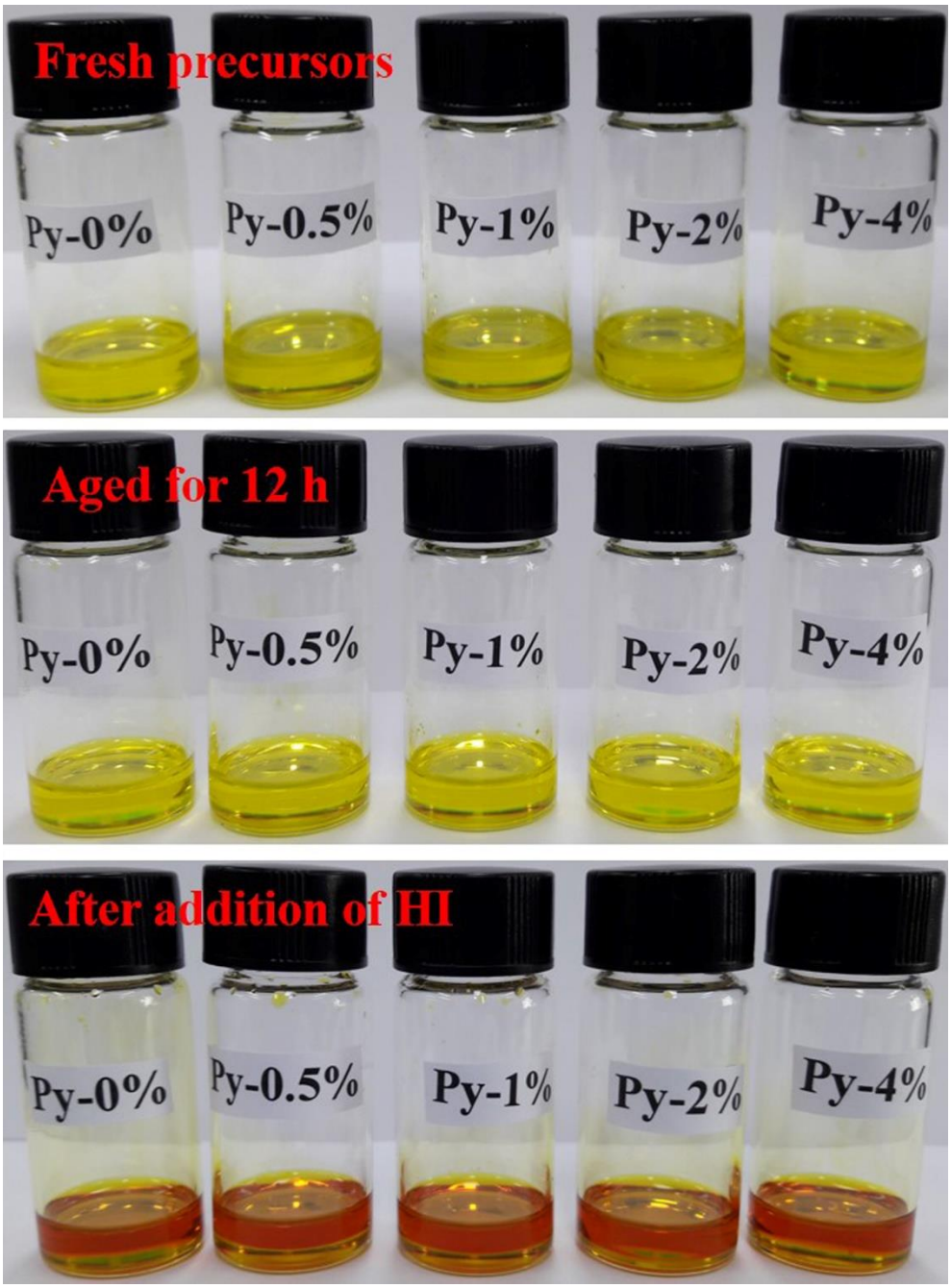

Figure S1. Photographs of perovskite precursors with different contents of Py additive. Top row: fresh precursors; middle row: after aging for 12 h; bottom row: after addition of HI solution into the above 12h-aged precursors.

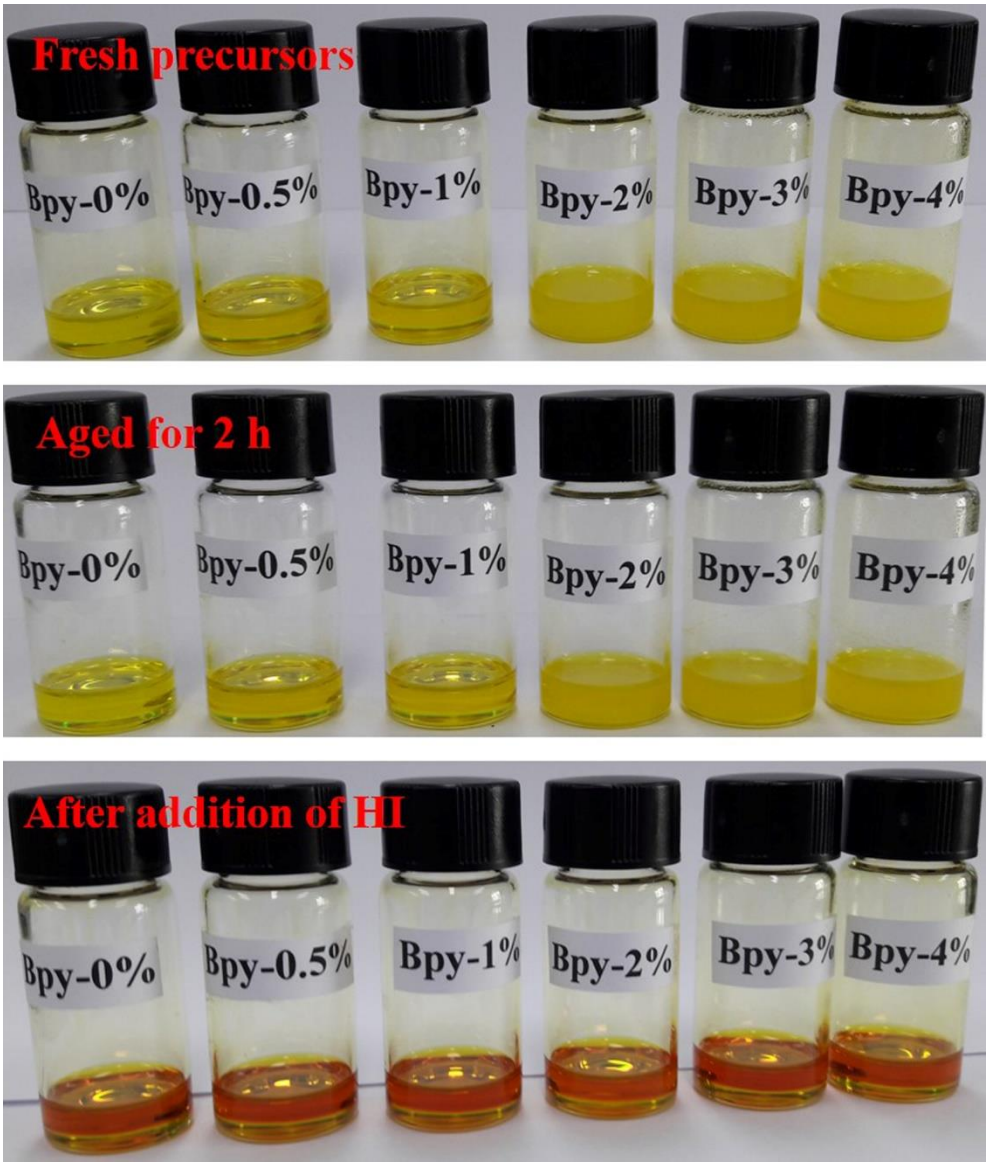

Figure S2. Photographs of perovskite precursors with different contents of Bpy additive. Top row: fresh precursors; middle row: after aging for 2 h; bottom row: after addition of HI solution into the above 2h-aged precursors.

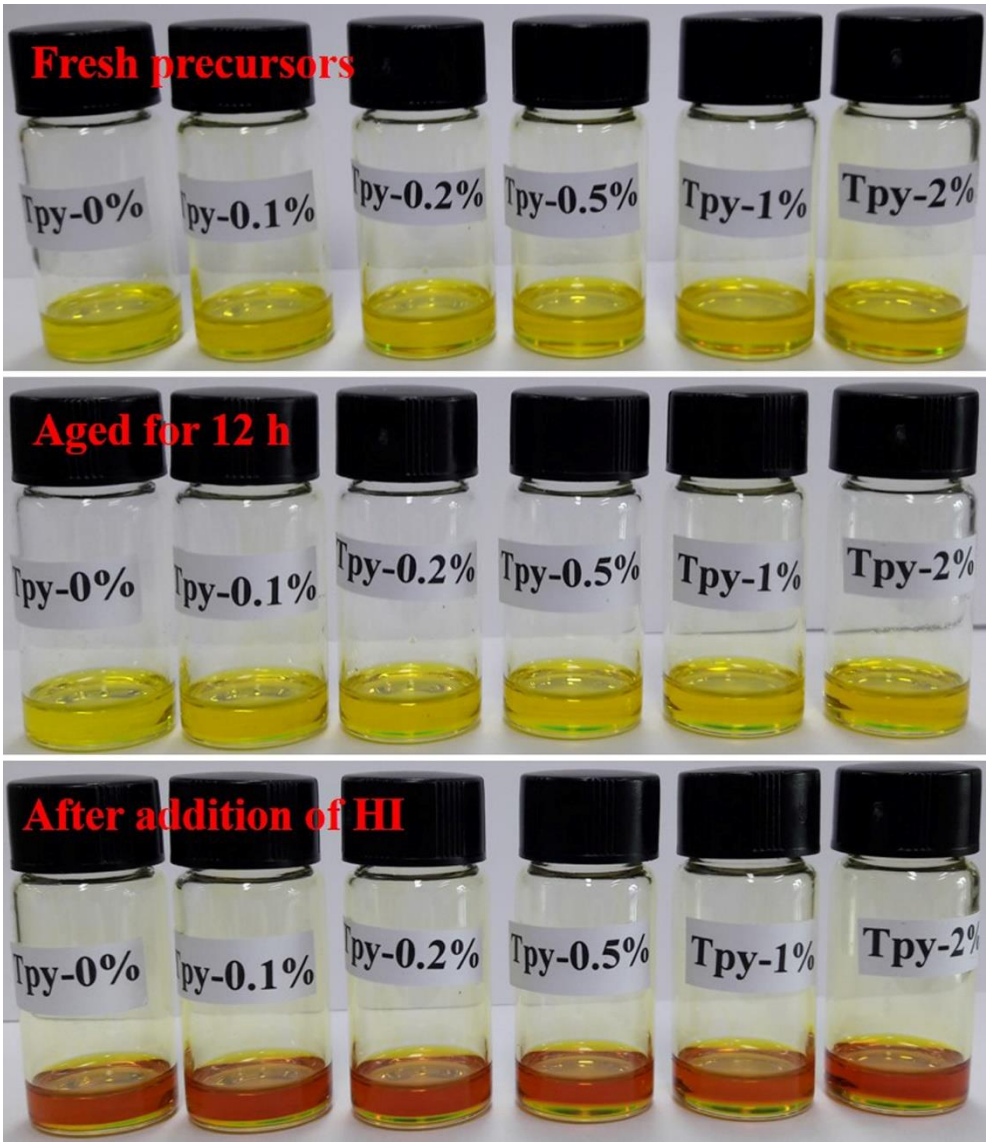

Figure S3. Photographs of perovskite precursors with different contents of Tpy additive. Top row: fresh precursors; middle row: after aging for 12 h; bottom row: after addition of HI solution into the above 12h-aged precursors.

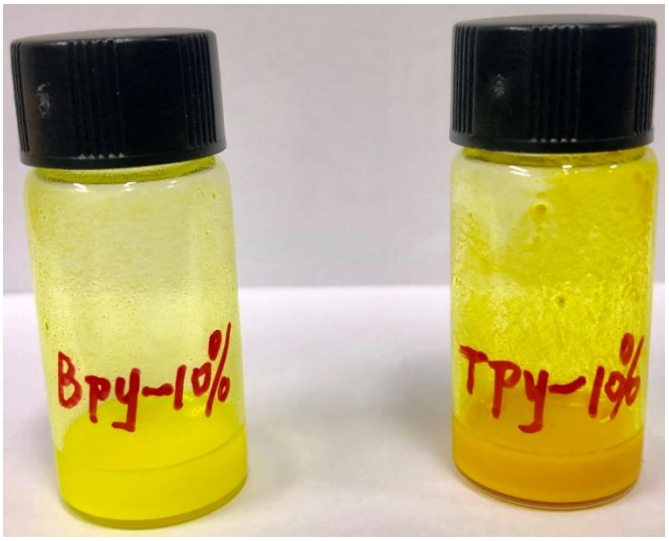

Figure S4. Photographs of perovskite precursors with 10% Bpy (left) and 10% Tpy additive (right).

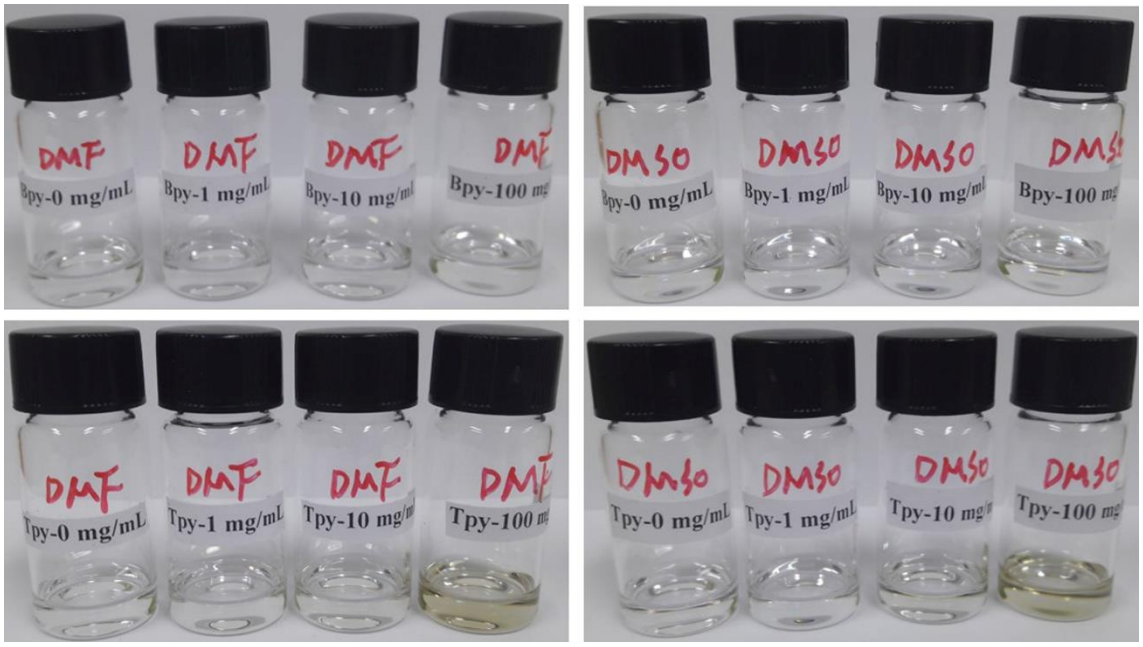

Figure S5. Photographs of different concentrations of Bpy or Tpy in DMF or DMSO solvent.

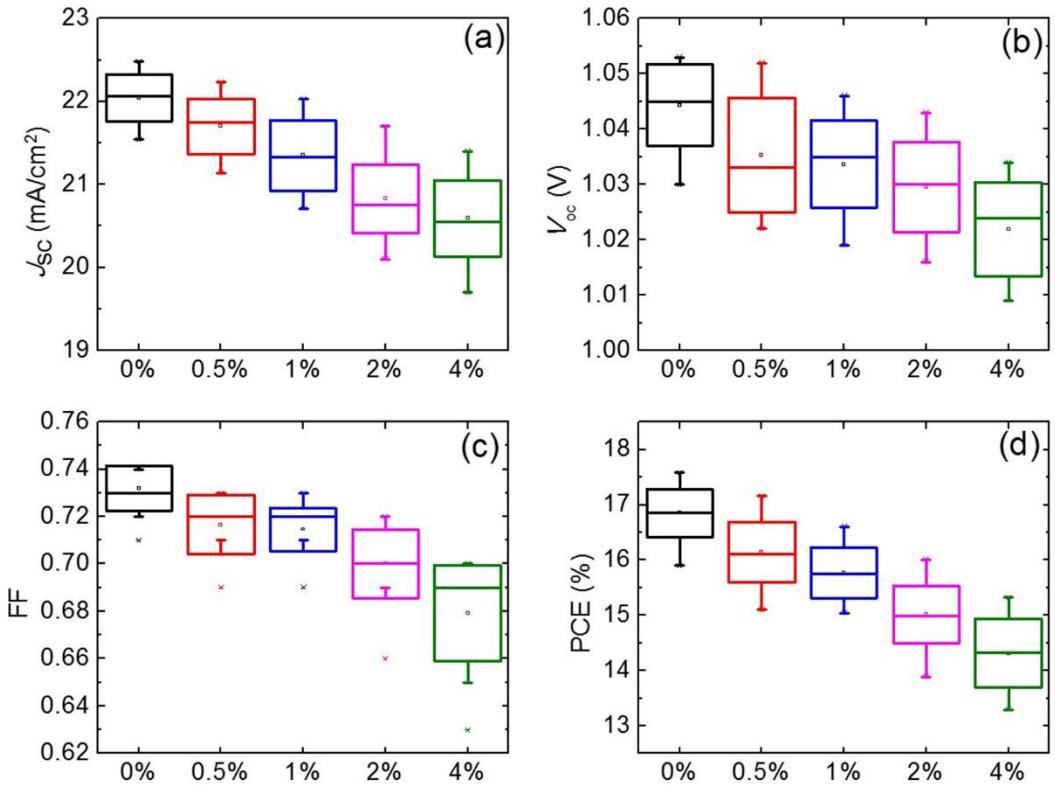

Figure S6. Statistic (a) J_{sc}, (b) V_{oc}, (c) FF and (d) PCE of devices containing different ratio of Py additive. The statistical data were collected from 15 cells for each kind of concentration. *J-V* curves were measured in reverse scan (RS) with a scan rate of 130 mV/s under simulated AM 1.5G one sun illumination of 100 mW/cm^2.

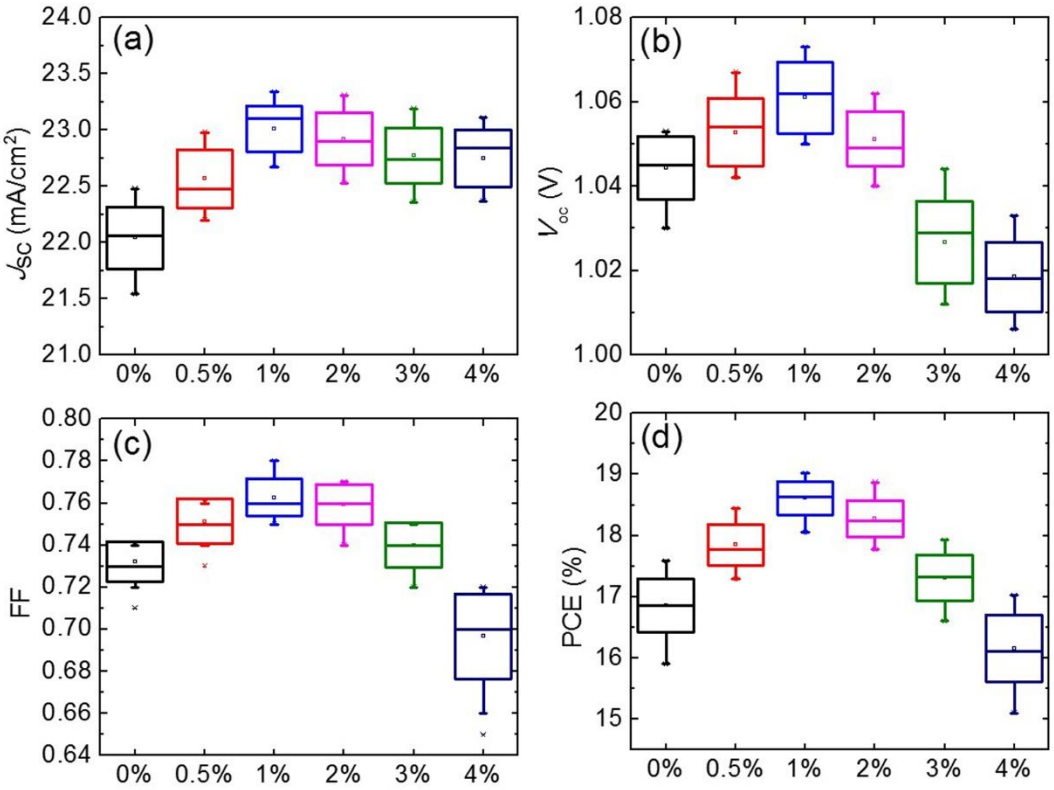

Figure S7. Statistic (a) J_{sc}, (b) V_{oc}, (c) FF and (d) PCE of devices containing different ratio of Bpy additive. The statistical data were collected from 15 cells for each kind of concentration. *J-V* curves were measured in reverse scan (RS) with a scan rate of 130 mV/s under simulated AM 1.5G one sun illumination of 100 mW/cm^2.

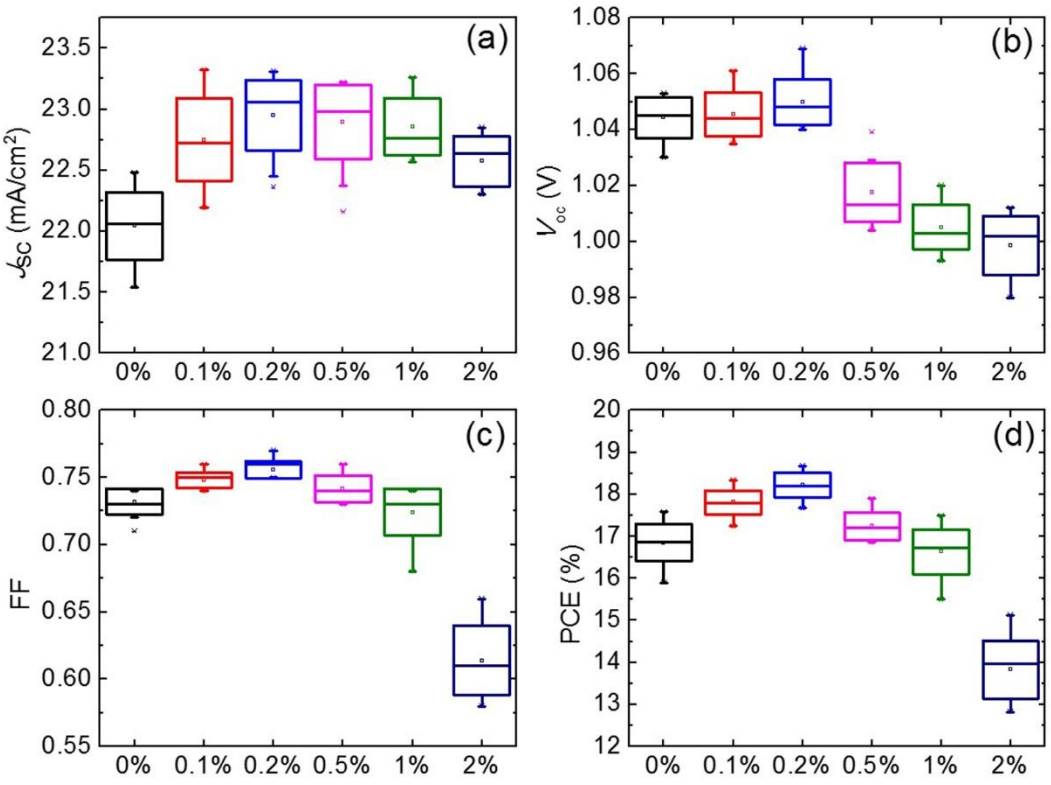

Figure S8. Statistic (a) J_{sc}, (b) V_{oc}, (c) FF and (d) PCE of devices containing different ratio of Tpy additive. The statistical data were collected from 15 cells for each kind of concentration. *J*-*V* curves were measured in reverse scan (RS) with a scan rate of 130 mV/s under simulated AM 1.5G one sun illumination of 100 mW/cm^2.

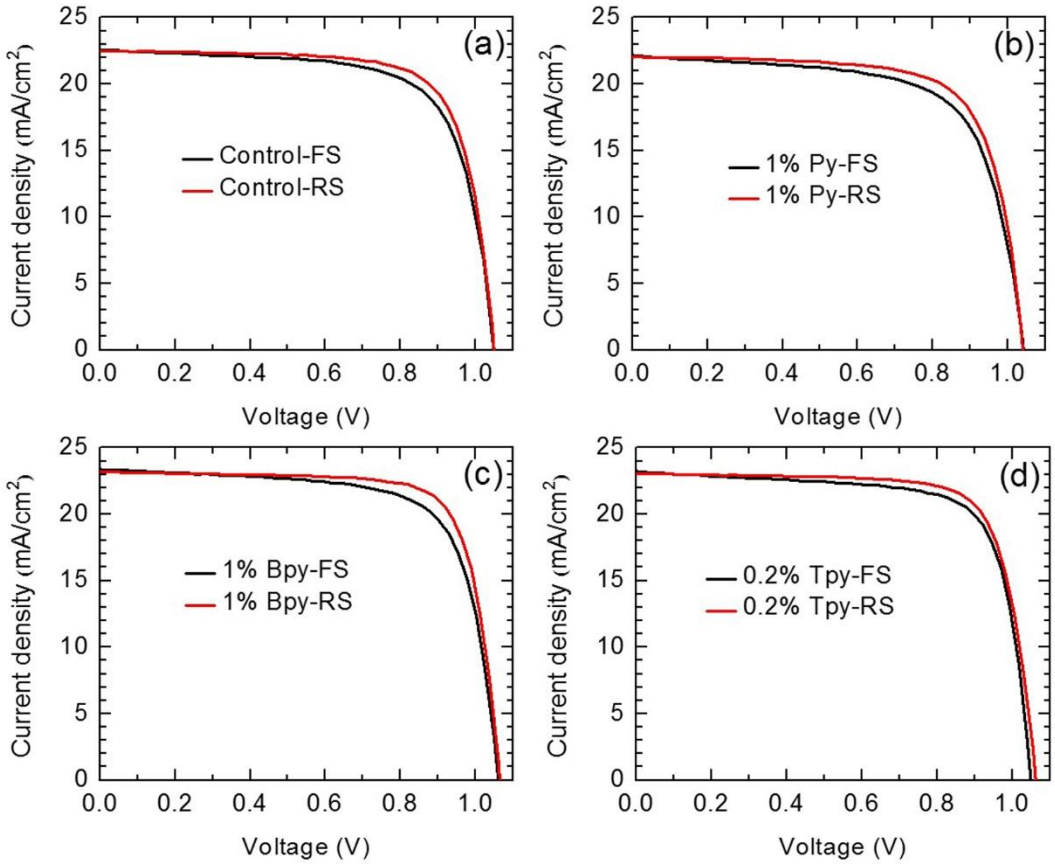

Figure S9. *J-V* curves of control, Py-1%, Bpy-1%, and Tpy-0.2% devices measured in reverse scan (RS) and forward scan (FS) with a scan rate of 130 mV/s under simulated AM 1.5G one sun illumination of 100 mW/cm^2.

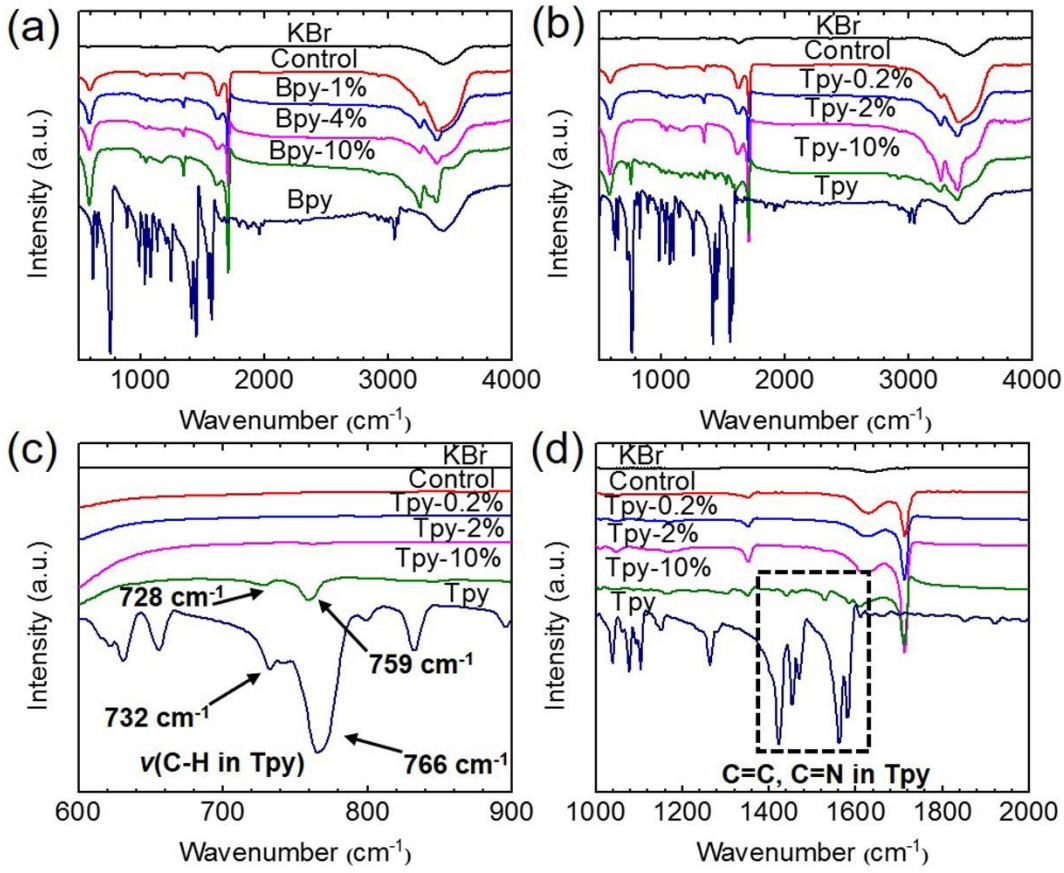

Figure S10. (a) FTIR spectra of KBr, control, Bpy-1%, Bpy-4%, Bpy-10%, and Bpy. FTIR spectra of KBr, control, Tpy-0.2%, Tpy-2%, Tpy-10%, and Tpy: (b) 500-4000 cm^{-1}; (c) 600-900 cm^{-1}; (d) 1000-2000 cm^{-1}.

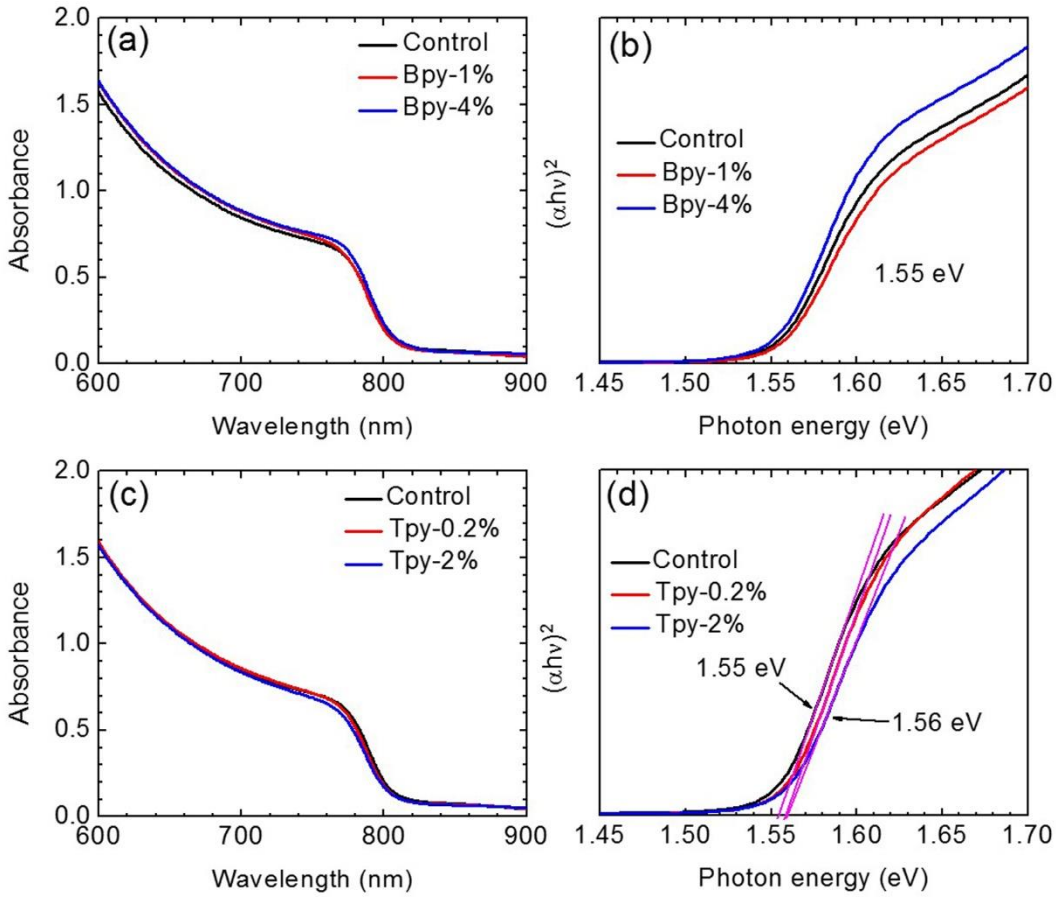

Figure S11. (a) UV−vis absorption spectra and (b) $(\alpha hv)^2$ as a function of photon energy of control, Bpy-1%, and Bpy-4% films deposited on mp-TiO_2/bl-TiO_2/FTO/glass substrates. (c) UV−vis absorption spectra and (d) $(\alpha hv)^2$ as a function of photon energy of control, Tpy-0.2%, and Tpy-2% films deposited on mp-TiO_2/bl-TiO_2/FTO/glass substrates.

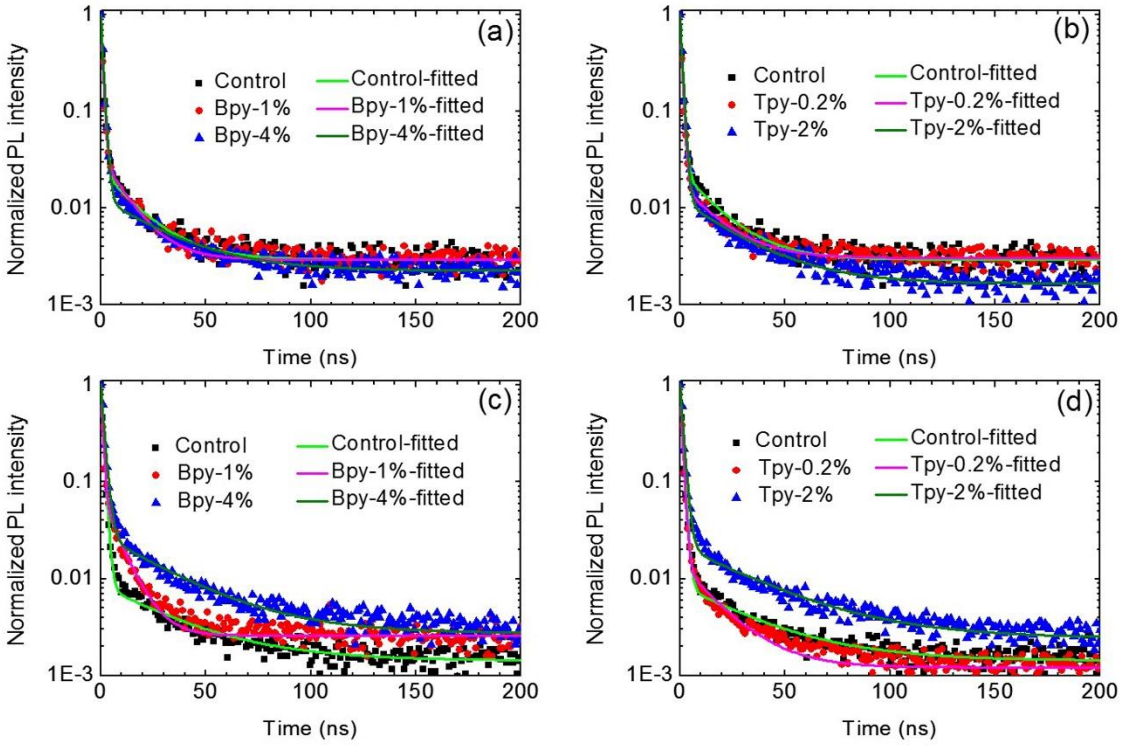

Figure S12. TRPL spectra of control, Bpy-1%, and Bpy-4% perovskite films with (a) spiro-MeOTAD layer and (c) FTO/bl-TiO_2/mp-TiO_2 layers. TRPL spectra of control, Tpy-0.2%, and Tpy-2% perovskite films with (b) spiro-MeOTAD layer and (d) FTO/bl-TiO_2/mp-TiO_2 layers.

Table S1. Photovoltaic performance parameters of devices containing different ratio of Py additive. The statistical data were collected from 15 cells for each kind of concentration. *J-V* curves were measured in reverse scan (RS) with a scan rate of 130 mV/s under simulated AM 1.5G one sun illumination of 100 mW/cm^2.

Ratio of Py		J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
0%	Champion	22.48	1.050	0.74	17.58
	Average	22.04±0.28	1.044±0.007	0.73±0.01	16.85±0.44
0.5%	Champion	22.23	1.052	0.73	17.16
	Average	21.70±0.34	1.035±0.010	0.72±0.01	16.14±0.55
1%	Champion	22.03	1.042	0.72	16.58
	Average	21.35±0.42	1.034±0.008	0.71±0.01	15.77±0.46
2%	Champion	21.70	1.019	0.72	16.01
	Average	20.83±0.41	1.030±0.008	0.70±0.01	15.01±0.52
4%	Champion	21.40	1.022	0.70	15.32
	Average	20.59±0.46	1.022±0.008	0.68±0.02	14.31±0.62

Table S2. Photovoltaic performance parameters of devices containing different ratio of Bpy additive. The statistical data were collected from 15 cells for each kind of concentration. *J-V* curves were measured in reverse scan (RS) with a scan rate of 130 mV/s under simulated AM 1.5G one sun illumination of 100 mW/cm^2.

Ratio of Bpy		J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
0%	Champion	22.48	1.050	0.74	17.58
	Average	22.04±0.28	1.044±0.007	0.73±0.01	16.85±0.44
0.5%	Champion	22.98	1.054	0.76	18.44
	Average	22.57±0.26	1.053±0.008	0.75±0.01	17.84±0.33
1%	Champion	23.17	1.066	0.77	19.02
	Average	23.01±0.20	1.061±0.008	0.76±0.01	18.61±0.27
2%	Champion	23.07	1.062	0.77	18.87
	Average	22.92±0.23	1.051±0.006	0.76±0.01	18.28±0.30
3%	Champion	23.00	1.044	0.75	17.93
	Average	22.78±0.25	1.027±0.010	0.74±0.01	17.31±0.37
4%	Champion	23.10	1.018	0.72	17.02
	Average	22.75±0.25	1.018±0.008	0.70±0.02	16.15±0.54

Table S3. Photovoltaic performance parameters of devices containing different ratio of Tpy additive. The statistical data were collected from 15 cells for each kind of concentration. *J-V* curves were measured in reverse scan (RS) with a scan rate of 130 mV/s under simulated AM 1.5G one sun illumination of 100 mW/cm^2.

Ratio of Tpy		J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
0%	Champion	22.48	1.050	0.74	17.58
	Average	22.04±0.28	1.044±0.007	0.73±0.01	16.85±0.44
0.1%	Champion	23.10	1.058	0.75	18.34
	Average	22.75±0.34	1.045±0.008	0.75±0.01	17.80±0.29
0.2%	Champion	23.07	1.062	0.76	18.68
	Average	22.95±0.29	1.050±0.008	0.76±0.01	18.21±0.29
0.5%	Champion	22.98	1.020	0.76	17.90
	Average	22.89±0.31	1.017±0.010	0.74±0.01	17.24±0.33
1%	Champion	23.26	1.017	0.74	17.49
	Average	22.86±0.24	1.005±0.008	0.72±0.02	16.63±0.54
2%	Champion	22.79	1.004	0.66	15.13
	Average	22.57±0.20	0.999±0.011	0.61±0.03	13.83±0.69

Table S4. Photovoltaic performance parameters of control, Py-1%, Bpy-1%, and Tpy-0.2% devices measured in reverse scan (RS) and forward scan (FS) with a scan rate of 130 mV/s under simulated AM 1.5G one sun illumination of 100 mW/cm^2.

Devices		J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
Control device	FS	22.57	1.050	0.71	16.77
	RS	22.48	1.050	0.74	17.58
Py-1%	FS	22.18	1.043	0.68	15.66
	RS	21.97	1.046	0.72	16.61
Bpy-1%	FS	23.36	1.061	0.72	17.77
	RS	23.17	1.066	0.77	19.02
Tpy-0.2%	FS	23.23	1.051	0.74	17.97
	RS	23.07	1.062	0.76	18.68

Table S5. Fitted results of TRPL curves in Figure 7 and Figure S10 using a bi-exponential decay equation of $I(t) = I_0 + A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$, where τ_1 and τ_2 represent fast and slow decay time constant, respectively. τ_{Ave} was calculated using relation of $\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

Sample	Devices	Control		Bpy-1%		Bpy-4%		Tpy-0.2%		Tpy-2%	
glass/perovskite		τ_1	τ_2	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2
	τ(ns)	1.84	138.44	1.94	258.44	1.47	116.90	1.58	232.56	1.74	87.36
	%	89.8	10.2	72.0	28.0	91.5	8.5	85.5	14.5	83.8	16.2
	τ_{ave}(ns)	124.14		253.58		103.14		223.68		79.36	
glass/perovskite/ spiro-MeOTAD		τ_1	τ_2	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2
	τ(ns)	0.95	16.34	0.82	11.57	1.05	27.32	0.87	16.11	1.04	25.71
	%	97.9	2.1	96.8	3.2	98.9	1.1	98.5	1.5	98.9	1.1
	τ_{ave}(ns)	5.10		4.24		6.95		4.22		6.36	
glass/FTO/bl-TiO_2/mp-TiO_2/perovskite		τ_1	τ_2	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2
	τ(ns)	1.10	33.34	0.86	8.09	1.51	31.53	0.96	16.77	1.43	36.65
	%	99.3	0.7	93.0	7.0	97.4	2.6	98.7	1.3	98.0	2.0
	τ_{ave}(ns)	6.78		3.86		12.23		3.92		13.52	

Table S6. Capacitance (C), V_{TFL}, dielectric constant (ε), trap density (n_t), and area (A) of perovskite films with different concentrations of Bpy and Tpy additives.

Device ID	C ($\times 10^{-8}$ F)	V_{TFL} (V)	ε	Area (cm^2)	n_t ($\times 10^{16}$ cm^{-3})
Control	1.41	0.731	36.77	0.195	1.47
Bpy-1%	1.44	0.384	38.54	0.190	0.81
Bpy-4%	1.45	0.765	38.40	0.192	1.60
Tpy-0.2%	1.45	0.448	38.80	0.190	0.95
Tpy-2%	1.43	0.831	37.48	0.194	1.70