Supplementary Information

$FAPbBr_3$ perovskite solar cells with V_{OC} over 1.5 V by controlled crystal growth using a tetramethylenesulfoxide

Youhei Numata[,a] Naoyuki Shibayama[b] and Tsutom Miyasaka*[,b]*

[a] Research Center for Advanced Science and Technology (RCAST), The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904 Japan

[b] Department of Engineering, Toin University of Yokohama, 1614 Kurgane-cho, Aoba, Yokohama, Kanagawa 225-8503 Japan.

Table S1. Photovoltaic parameters of $FAPbBr_3$ PSCs with different TMSO concentrations in DMSO solvent. Device architecture: FTO/TiO_2 CL/TiO_2 meso/$FAPbBr_3$/spiro/Au.

TMSO content in DMSO (%)	scan direction	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF*	PCE (%)
0	forward	4.87 ± 0.16	1.32 ± 0.05	0.49 ± 0.02	3.15 ± 0.18
	reverse	4.85 ± 0.10	1.31 ± 0.06	0.54 ± 0.01	3.45 ± 0.19
5	forward	6.01 ± 0.14	1.30 ± 0.03	0.49 ± 0.02	3.80 ± 0.26
	reverse	5.78 ± 0.06	1.32 ± 0.04	0.52 ± 0.01	3.99 ± 0.16
10	forward	6.08 ± 0.14	1.30 ± 0.01	0.49 ± 0.03	3.91 ± 0.32
	reverse	5.71 ± 0.10	1.35 ± 0.01	0.56 ± 0.03	4.28 ± 0.26
20	forward	6.31 ± 0.11	1.28 ± 0.02	0.51 ± 0.01	4.11 ± 0.20
	reverse	6.04 ± 0.11	1.31 ± 0.02	0.54 ± 0.01	4.25 ± 0.19

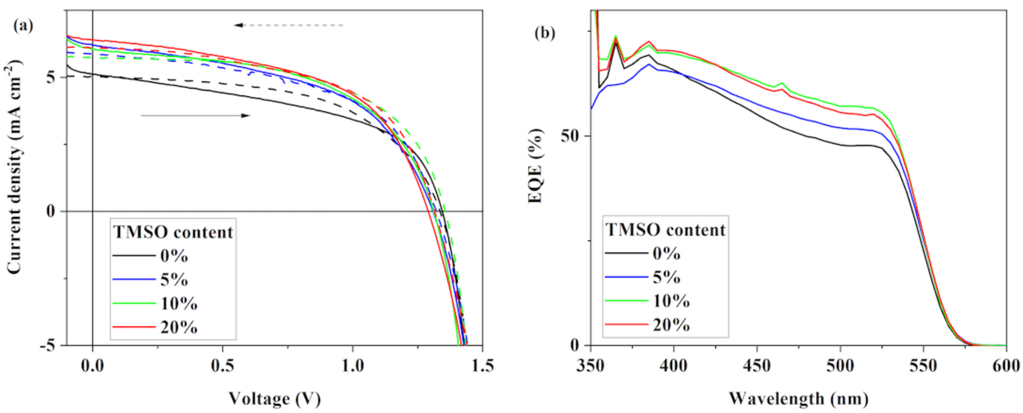

Fig. S1 (a) *J-V* curves and (b) EQE spectra of $FAPbBr_3$ PSCs with different TMSO content. Device architecture: FTO/TiO_2 CL/TiO_2 meso/$FAPbBr_3$/spiro/Au.

Note. Above PSCs were not conducted Li-treatment of TiO_2 mesoporous layer and insertion of PMMA blocking layer.

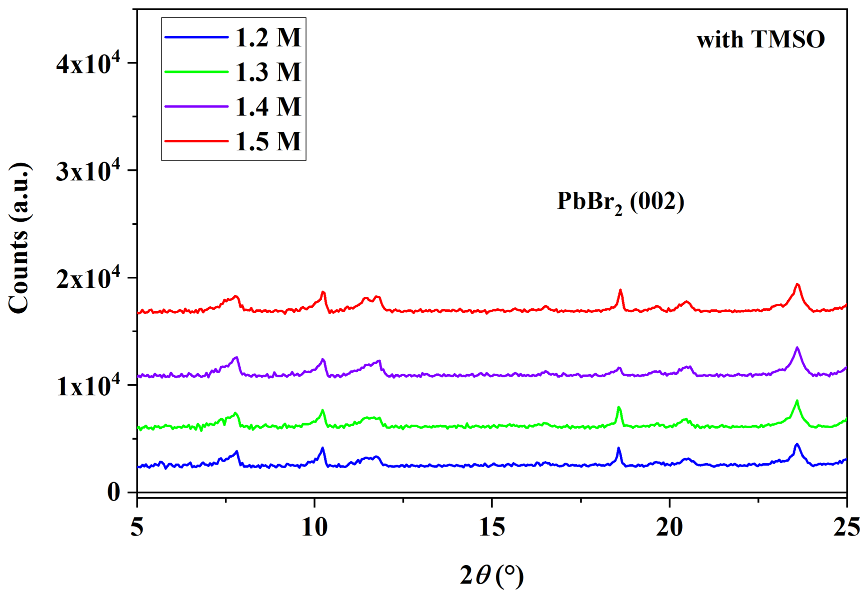

Fig. S2 XRD chart of $PbBr_2$–TMSO films prepared on Li-treated TiO_2 mesoporous layer; vertical axis was enlarged 100 times from **Fig. 1a**.

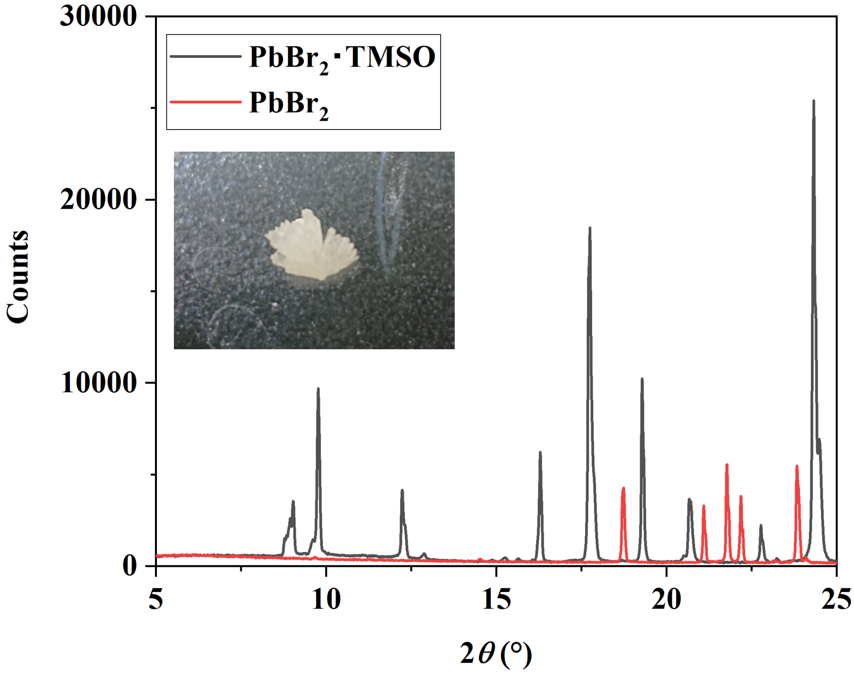

Fig. S3 XRD chart of ground $PbBr_2$•TMSO single crystal and $PbBr_2$ powder. Inset: photograph of $PbBr_2$•TMSO single crystals.

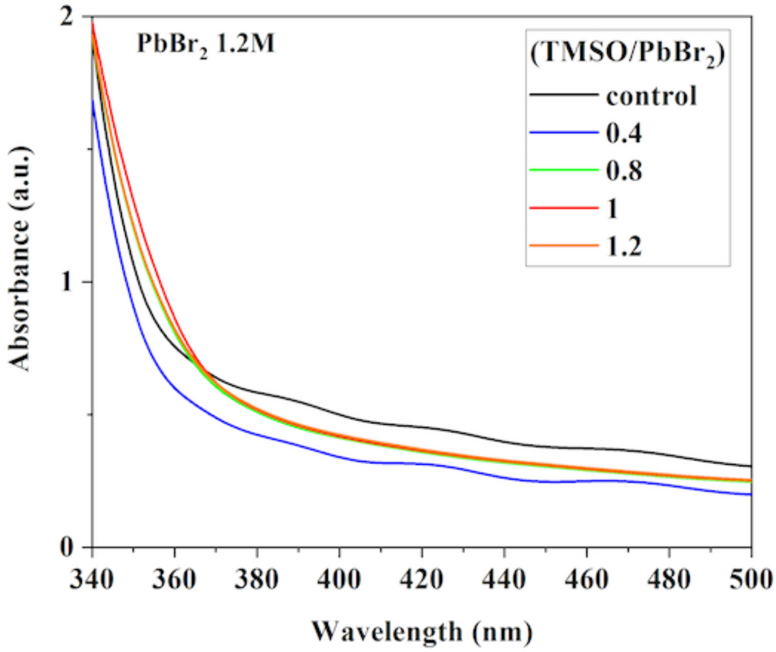

Fig. S4 UV spectra of $PbBr_2$ films with different concentration of TMSO in DMSO solvent. The $PbBr_2$ films were prepared on a Li-treated TiO_2 mesoporous film.

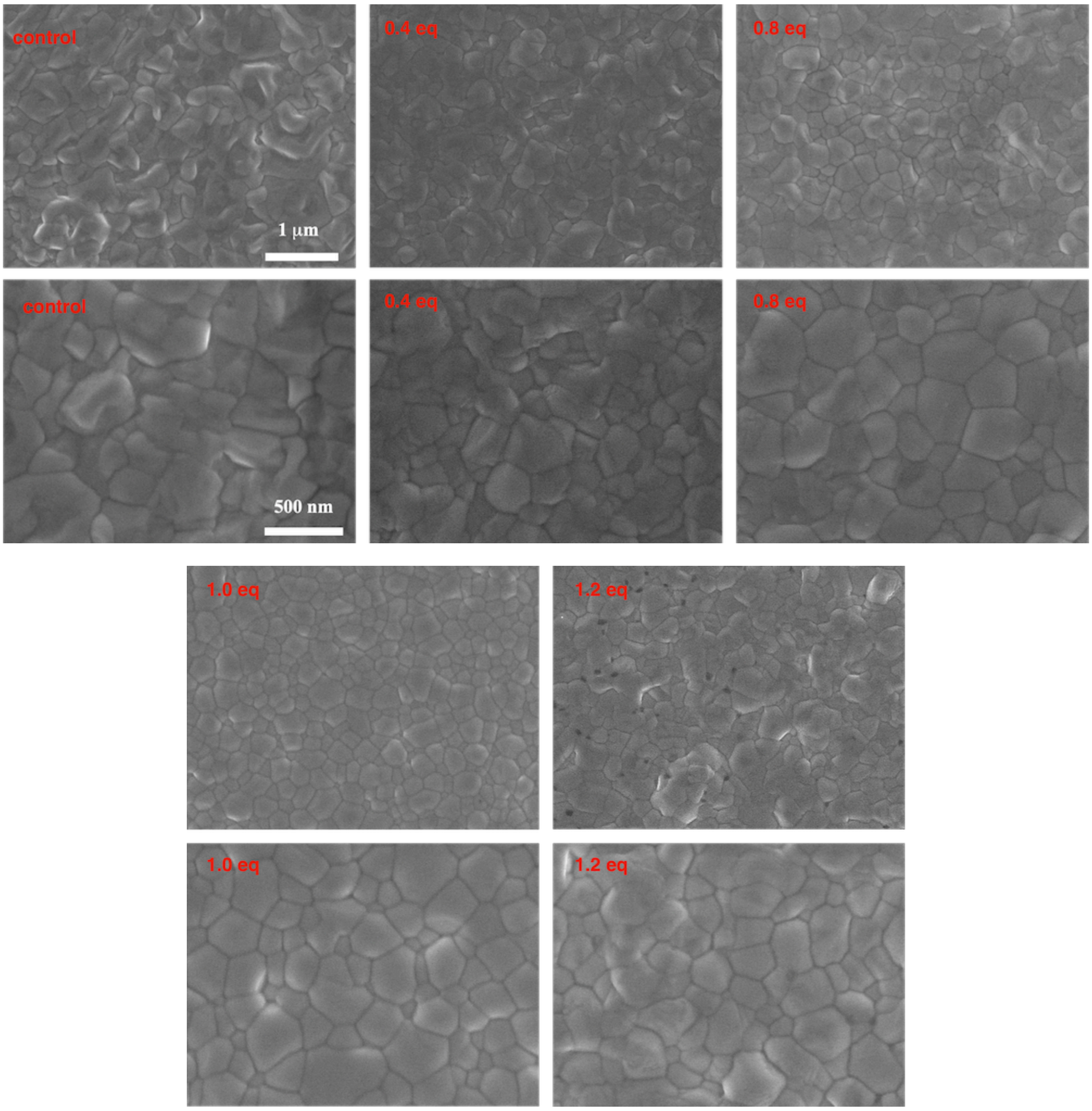

Fig. S5 surface SEM images of $FAPbBr_3$ films with different concentration of TMSO. The $FAPbBr_3$ films were prepared on a Li-treated TiO_2 mesoporous film.

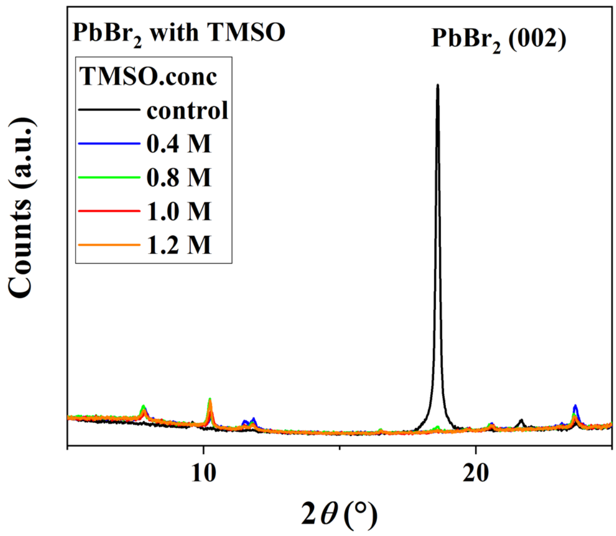

Fig. S6 XRD chart of $PbBr_2$ films with different concentration of TMSO in DMSO solvent.

Table S2. Photovoltaic parameters of $FAPbBr_3$ PSCs with and w/o TMSO

TMSO	$PbBr_2$ conc. (M)	Scan direction	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)
w/o	1.0	forward	3.49 ± 0.46	1.42 ± 0.02	0.44 ± 0.04	2.19 ± 0.44
		reverse	3.27 ± 0.45	1.41 ± 0.05	0.43 ± 0.02	1.98 ± 0.37
	1.2	forward	5.55 ± 0.15	1.38 ± 0.02	0.60 ± 0.03	4.59 ± 0.28
		reverse	5.36 ± 0.14	1.41 ± 0.02	0.56 ± 0.04	4.21 ± 0.36
	1.3	forward	5.56 ± 0.34	1.35 ± 0.02	0.61 ± 0.04	4.63 ± 0.49
		reverse	5.29 ± 0.34	1.36 ± 0.02	0.66 ± 0.04	4.73 ± 0.35
	1.4	forward	5.74 ± 0.38	1.35 ± 0.02	0.57 ± 0.04	4.48 ± 0.57
		reverse	5.35 ± 0.28	1.34 ± 0.04	0.68 ± 0.08	4.86 ± 0.72
with	1.2	forward	6.41 ± 0.13	1.45 ± 0.02	0.59 ± 0.03	5.50 ± 0.38
		reverse	6.12 ± 0.14	1.47 ± 0.02	0.61 ± 0.04	5.50 ± 0.46
	1.3	forward	6.53 ± 0.23	1.43 ± 0.03	0.60 ± 0.06	5.62 ± 0.73
		reverse	6.17 ± 0.31	1.47 ± 0.02	0.66 ± 0.05	5.95 ± 0.58
	1.4	forward	7.05 ± 0.13	1.13 ± 0.07	0.48 ± 0.08	3.81 ± 0.82
		reverse	6.53 ± 0.36	1.24 ± 0.08	0.59 ± 0.04	4.72 ± 0.45
	1.5	forward	6.93 ± 0.46	1.08 ± 0.11	0.48 ± 0.09	3.60 ± 1.02
		reverse	6.47 ± 0.56	1.18 ± 0.07	0.59 ± 0.07	4.49 ± 0.73

Cell area: 0.25 cm^2 (5 × 5 mm^2), aperture area was defined with black metal mask. The parameters are average values of 12~18 cells

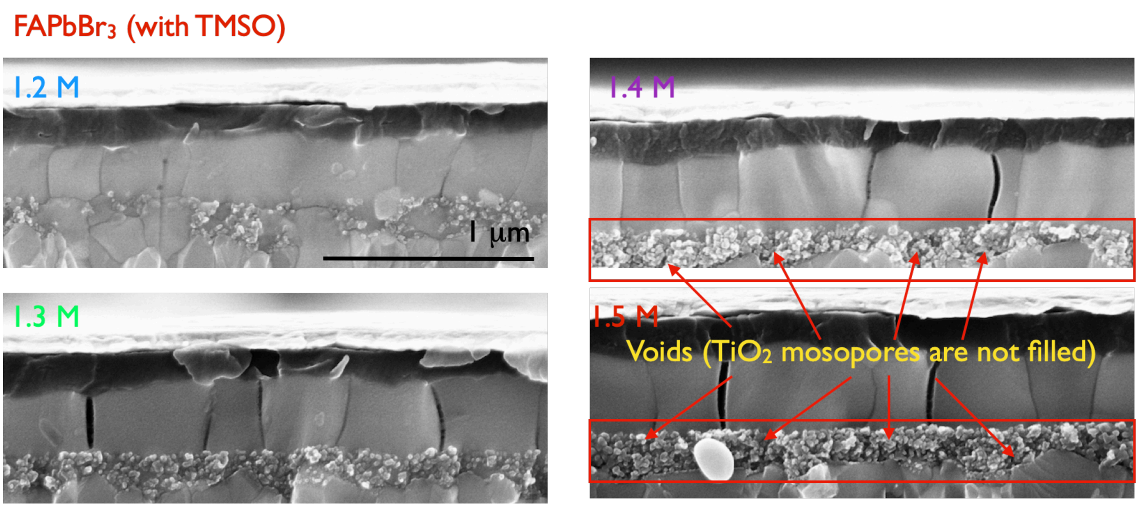

Fig. S7 Cross-sectional images of $FAPbBr_3$ (with TMSO) cells.

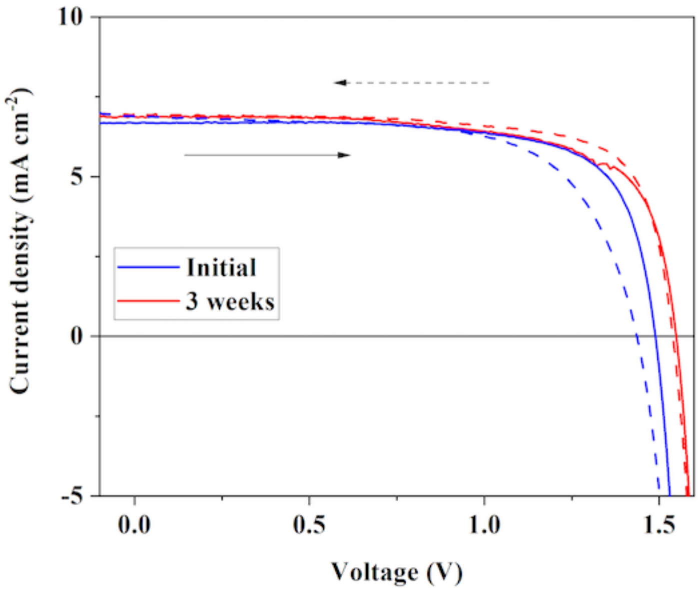

Fig. S8 Aging effect of $FAPbBr_3$ PSC based on a 1.3 M $PbBr_2$–TMSO precursor film stored under dark and dry condition for 3 weeks.

Table S3 Summary of reported high-voltage Br-rich 3-D perovskite-based solar cells with V_{OC} over 1.4 V

Device architecture	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	η (%)	method	Ref.
$MAPbBr_3$						
FTO/c-TiO_2/$MAPbBr_3$/ Carbon	1.535	7.10	0.70	7.63	one-step	1
FTO/bl-TiO_2/m-TiO_2/ $MAPbBr_3$/PIF8-TAA/Au	1.40	6.1	0.79	6.7	one-step	2
FTO/NiOx/MoOx/ $MAPbBr_3$/ZrO/$PC_{61}BM$/Al	1.653	7.72	0.79	10.08	one-step	3
FTO/c-TiO_2/m-TiO_2/ $MAPbBr_3$/PTAA/Au	1.4	6.4	74	6.6	two-step	4
$FAPbBr_3$						
ITO/P3CT/$FAPbBr_3$/ PCBM/C_{60}/BCP/Cu	1.49	8.98	66.74	8.93	two-step	5
FTO/SnO_2/$FAPbBr_3$/spiro/Au	1.552	8.94	0.76	10.61	two-step	6
FTO/c-TiO_2/Li-m-TiO_2/ $FAPbBr_3$/spiro/Au	1.53	7.3	0.71	8.2	two-step	7
FTO/c-TiO_2/m-TiO_2/ $FAPbBr_3$/spiro/Au	1.42	6.8	72	7.0	two-step	8
FTO/c-TiO_2/m-TiO_2/$FAPbBr_3$/ SO7/Au	1.50	6.9	69	7.1	two-step	9
FTO/NiO/$FAPbBr_3$/Mg-ZnO/ PCBM/BCP/Ag	1.44	8.92	0.71	9.06	one-step	10
FTO/TiO_2/Li-m-TiO_2/$FAPbBr_3$ /PMMA/spiro/Au cell area: 0.25 mm^2	1.53	6.96	0.74	7.88	two-step	This work
$CsPbBr_3$						
FTO/SnO_2/GQDs/ $CsPbBr_3$/Carbon	1.522	7.91	78.4	9.51	two-step	11
FTO/c-TiO_2/m-TiO_2/ Sm-$CsPbBr_3$/Carbon	1.594	7.48	85.1	10.14	two-step	12
FTO/c-TiO_2/m-TiO_2/ $CsPbBr_3$/Carbon	1.584	7.42	82.11	9.65	two-step	13
FTO/c-TiO_2/m-TiO_2/ $CsPbBr_3$/Carbon	1.432	7.86	81	6.78	two-step	14
FTO/c-TiO_2/Li-m-TiO_2/ $CsPbBr_3$/spiro/Au	1.45	5.97	70	6.19	two-step	15
FTO/c-TiO_2/m-TiO_2/ $CsPbBr_3$/spiro/Au	1.43	8.85	0.62	7.86	two-step	16
FTO/c-TiO_2/m-TiO_2/ m-ZrO_2/$CsPbBr_3$/Carbon	1.44	7.75	73.52	8.19	two-step	17
FTO/c-TiO_2/m-TiO_2/ $CsPbBr_3$/P3HT-ZnPc/ Carbon	1.578	7.652	83.06	10.03	two-step	18
FTO/ZnO/ $CsPbBr_3$-$CsPb_2Br_5$/spiro/Au	1.43	6.17	77.2	6.31	two-step	19
ITO/c-TiO_2/$CsPbBr_3$/ Carbon	1.51	7.3	0.75	8.3	mist-CVD	20

FTO/c-TiO_2/m-TiO_2/ $CsPbBr_3$-L-lysine/Carbon	1.565	7.64	81.0	9.68	two-step	21
FTO/c-TiO_2/Sb-TiO_2/ $CsPbBr_3$/Carbon	1.654	6.70	80.4	8.91	two-step	22
FTO/c-TiO_2/m-TiO_2/ $CsPb_{0.97}Sr_{0.03}Br_3$/Carbon	1.54	7.71	81.1	9.63	two-step	23
FTO/c-TiO_2/m-TiO_2/ $CsPb_{0.97}Tb_{0.03}Br_3$/SnS:ZnS/ NiOx/Carbon	1.57	8.21	79.6	10.26	two-step	24
FTO/c-TiO_2/m-TiO_2/ $CsPbBr_3$/MnS/Carbon	1.52	8.28	0.83	10.45	two-step	25
FTO/c-TiO_2/m-TiO_2/ $CsPbBr_3$/Carbon-MWCNT	1.431	6.84	0.78	7.62	two-step	26
FTO/c-TiO_2/m-TiO_2/ $CsPbBr_3$/[BMMIM]Cl/ Carbon	1.61	7.45	83	9.92	two-step	27
FTO/c-TiO_2/m-TiO_2/ $CsPbBr_3$/Carbon	1.458	8.12	82.1	9.72	two-step	28
ITO/NiMgOx/PVP/ $CsPbBr_3$:AVAB/ CdSe QDs/ZnO/Al	1.73	3.5	N/A	N/A	two-step	29
FTO/L-TiO_2:$MoSe_2$/ $CsPbBr_3$/Carbon	1.615	7.88	78.7	10.02	two-step	30
FTO/c-TiO_2/m-TiO_2/GQDs/ $CsPbBr_3$/CISZ-QD/Carbon	1.522	7.35	84.3	9.43	two-step	31
FTO/N-TiO_2-NRA/ $CsPbBr_3$/Carbon	1.58	6.55	81.96	8.50	two-step	32
FTO/TiO_2/$CsPbBr_3$ QDs/ PTB7/MoO_3/Ag	1.61	3.5	75.95	4.28	QD spin-coat	33
$CsPbI_2Br$						
ITO/SnO_2/SnOx/$CsPbI_2Br$/ poly(DTSTPD-r-BThTPD)/Au	1.41	14.25	0.77	15.53	one-step	34
ITO/SnO_2/SnOx/$CsPbI_2Br$/ PDTDT/Au	1.42	15.02	81.29	17.36	one-step	35

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