

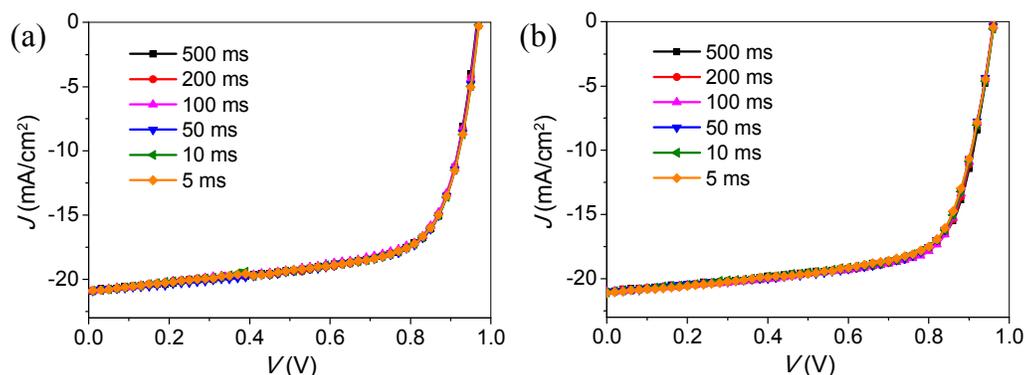
## Supporting Information

### Triple Cathode Buffer Layers Composed of PCBM, C<sub>60</sub> and LiF for High Performance Planar Perovskite Solar Cells

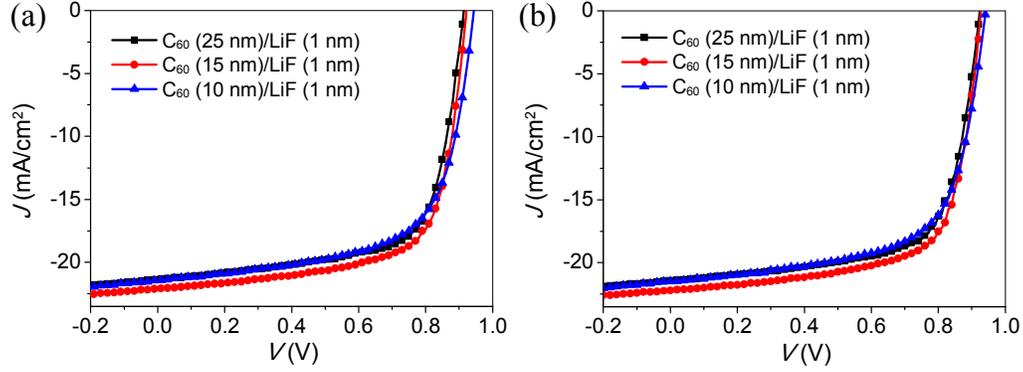
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**Figure S1**  $J$ - $V$  characteristics of the planar  $p-i-n$  PSCs with PCBM/LiF (1 nm) CBLs measured by (a)FS and (b)RS with different delay times after each 10 mV voltage step under the illumination of AM 1.5 G, 100 mW/cm<sup>2</sup>.



**Figure S2** Effect of  $C_{60}$  layer thickness on  $J$ - $V$  curves of the  $p$ - $i$ - $n$  PSCs with PCBM/ $C_{60}$ /LiF CBLs measured by (a) FS and (b) RS under the illumination of AM 1.5 G, 100 mW/cm<sup>2</sup>.

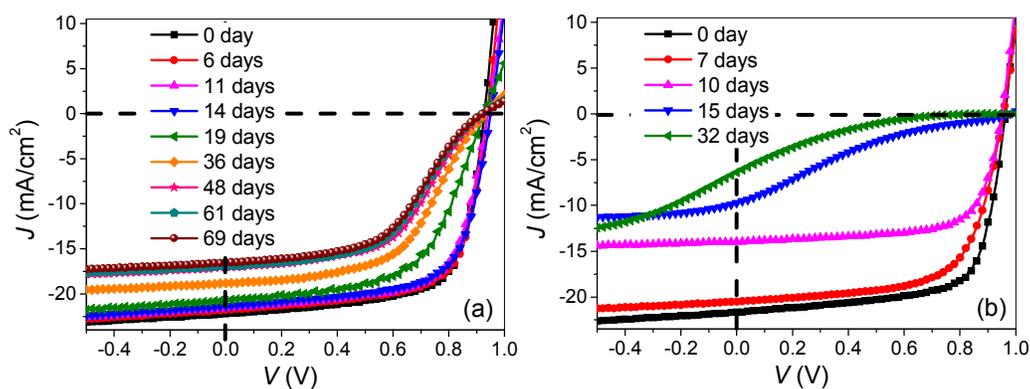
**Table S1** Effect of  $C_{60}$  layer thickness on the photovoltaic performance of the  $p$ - $i$ - $n$  PSCs with PCBM/ $C_{60}$ /LiF triple CBLs.

	CBL	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)	$R_s$ ( $\Omega$ cm <sup>2</sup> )	$R_{sh}$ ( $\Omega$ cm <sup>2</sup> )
FS	PCBM/ $C_{60}$ (25 nm)/LiF	21.34	0.91	68.9	13.45	3.74	330.67
	PCBM/ $C_{60}$ (15 nm)/LiF	22.08	0.92	69.2	14.09	3.12	357.79
	PCBM/ $C_{60}$ (10 nm)/LiF	21.42	0.94	64.9	13.12	3.86	310.76
RS	PCBM/ $C_{60}$ (25 nm)/LiF	21.42	0.92	68.7	13.59	3.87	352.52
	PCBM/ $C_{60}$ (15 nm)/LiF	22.21	0.93	69.2	14.24	3.14	368.53
	PCBM/ $C_{60}$ (10 nm)/LiF	21.49	0.94	65.0	13.15	3.98	317.13

**Table S2** Photovoltaic performance parameters of the *p-i-n* PSCs with different CBLs.

	CBL	$J_{sc}^{a)}$ (mA/cm <sup>2</sup> )	$V_{oc}^{a)}$ (V)	FF <sup>a)</sup> (%)	PCE <sup>a)</sup> (%)
FS	PCBM	18.87±0.42	0.94±0.03	61.5±1.7	10.98±0.51
	PCBM/LiF (1 nm)	21.58±0.10	0.95±0.01	70.6±0.3	14.52±0.14
	PCBM/LiF (5 nm)	20.08±0.61	0.91±0.01	56.6±3.3	10.32±0.83
	PCBM/C <sub>60</sub> (15 nm)/LiF (1 nm)	22.04±0.14	0.92±0.01	68.2±1.3	13.87±0.24
	PCBM/C <sub>60</sub> (15 nm)/LiF (5 nm)	21.92±0.13	0.94±0.01	65.9±1.2	13.61±0.13
	Ca	21.14±0.30	0.84±0.01	63.4±2.9	11.30±0.28
RS	PCBM	18.94±0.25	0.92±0.03	61.6±1.0	10.72±0.50
	PCBM/LiF (1 nm)	21.79±0.25	0.95±0.01	69.7±1.4	14.36±0.23
	PCBM/LiF (5 nm)	20.01±0.77	0.90±0.01	60.3±1.2	10.86±0.65
	PCBM/C <sub>60</sub> (15 nm)/LiF (1 nm)	22.09±0.20	0.92±0.01	68.4±1.4	13.97±0.30
	PCBM/C <sub>60</sub> (15 nm)/LiF (5 nm)	21.90±0.14	0.95±0.01	65.3±1.1	13.52±0.16
	Ca	21.19±0.24	0.84±0.02	66.8±0.68	11.95±0.31

<sup>a)</sup> Average values (for five devices) with standard deviation.



**Figure S3** Evolution of the  $J$ - $V$  curves, as a function of storage time in the glove box, for the devices with (a) PCBM/C<sub>60</sub> (15 nm)/LiF (1 nm) and (b) PCBM/LiF (1 nm) CBLs. These two devices were exposed to air for ~5 min after storage in the glove box for 15 (triple CBLs) and 11 days (double CBLs).