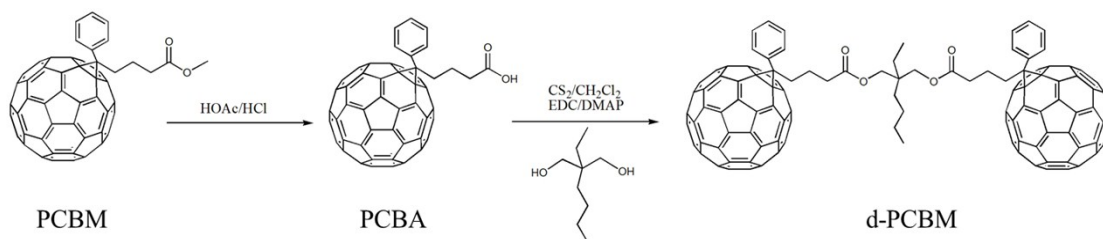


**Efficient promotion of charge separation and suppression of charge recombination by blending PCBM and its dimer as electron transport layer in inverted perovskite solar cells**

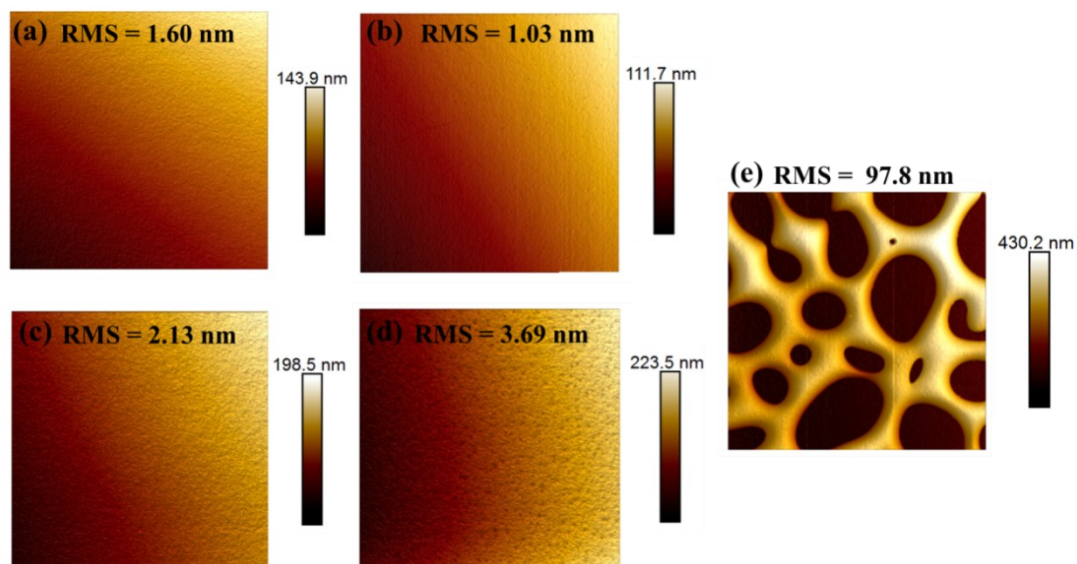
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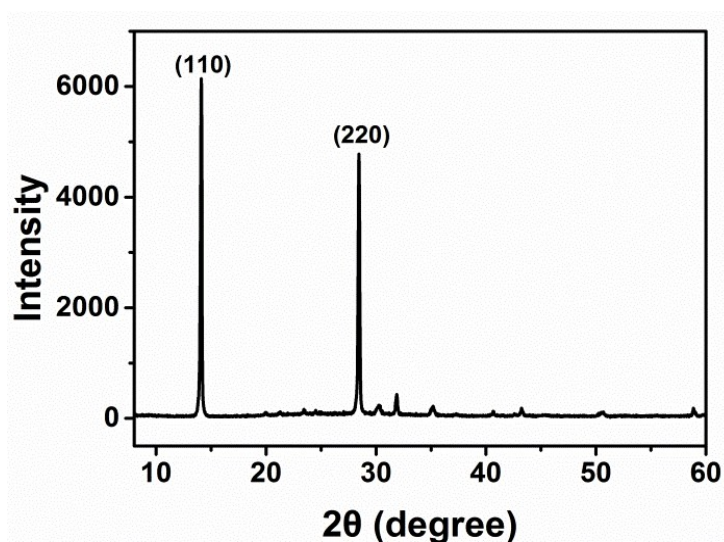
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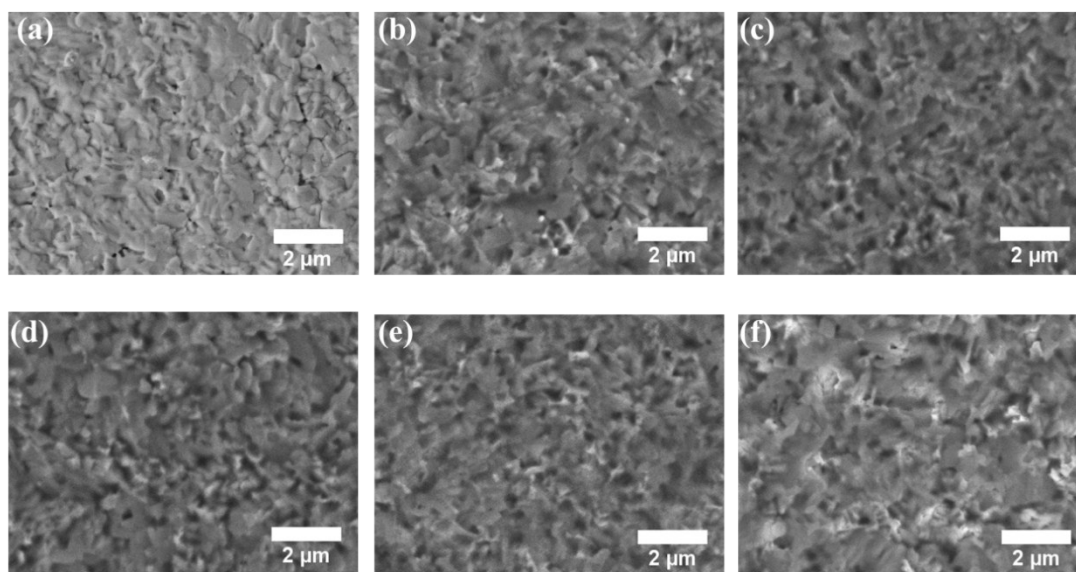
**Scheme S1** The synthetic route map of the dumb-belled PCBM dimer (d-PCBM).



**Figure S1** AFM images (size: 30×30 μm) of (a) PCBM film, (b) PCBM:d-PCBM (6:1) film, (c) PCBM:d-PCBM (4:1) film, (d) PCBM:d-PCBM (1:1) film and (e) d-PCBM film on quartz substrates.



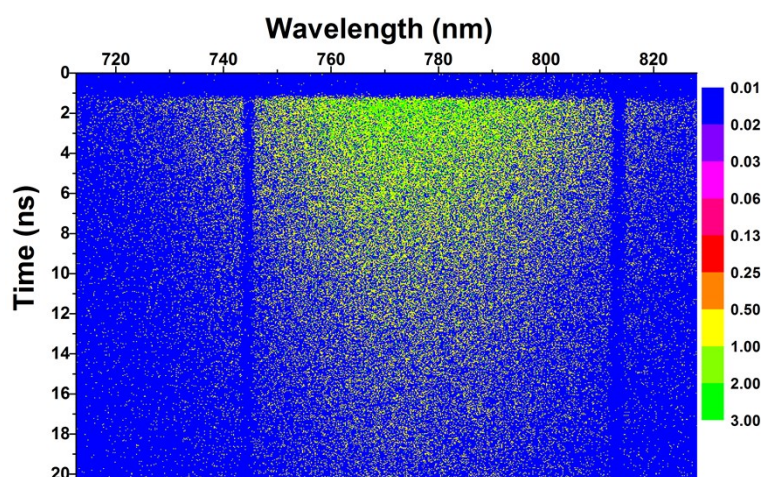
**Figure S2** XRD pattern of perovskite film on quartz substrate.



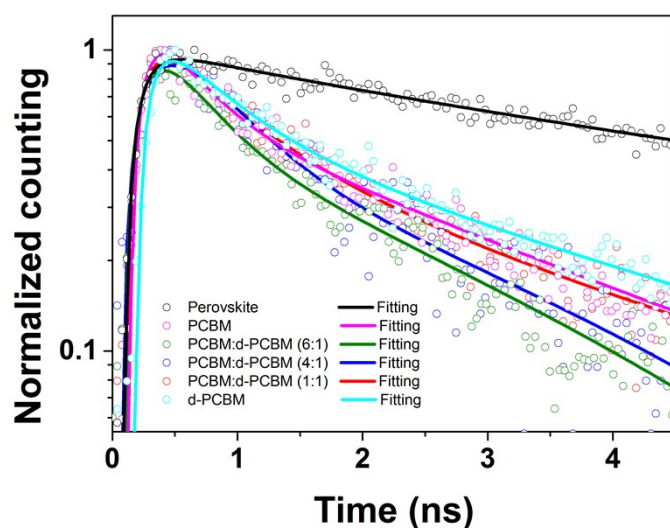
**Figure S3** SEM images of (a) perovskite film, (b) perovskite/PCBM film, (c) perovskite/PCBM:d-PCBM (6:1) film, (d) perovskite/PCBM:d-PCBM (4:1) film, (e) perovskite/PCBM:d-PCBM (1:1) film and (f) perovskite/d-PCBM film.

**Table S1** The peak positions of perovskite film and five different fullerene films coated perovskite layers from Gauss fitting the fluorescence spectra in Figure 3b.

Film Samples	Peak Position (nm)
Perovskite film	776
PCBM film	778
PCBM:d-PCBM (6:1) film	795
PCBM:d-PCBM (4:1) film	794
PCBM:d-PCBM (1:1) film	784
d-PCBM film	781



**Figure S4** Photoluminescence map of perovskite film on quartz substrate from streak camera measurement.



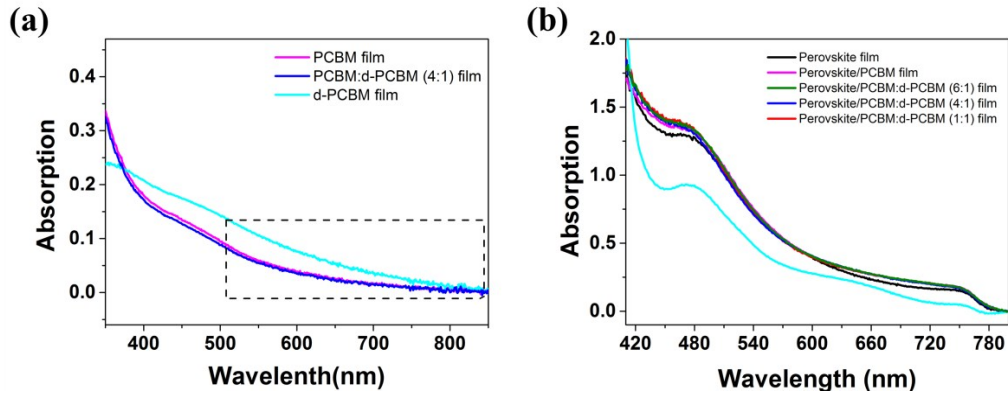
**Figure S5** Fluorescence dynamics of perovskite film and five different fullerene films coated perovskite layers extracted from streak camera measurement and related fitting curves.

**Table S2** Fluorescence decay lifetimes ( $\tau_{fl}$ ) extracted from fitting fluorescence dynamics of perovskite film and five different fullerene films coated perovskite layers.

Film Samples	$\tau_{fl}$ (ns)
Perovskite film	6.101
PCBM film	1.146
PCBM:d-PCBM (6:1) film	0.885
PCBM:d-PCBM (4:1) film	0.737
PCBM:d-PCBM (1:1) film	1.465
d-PCBM film	1.627

**Table S3** Charge separation efficiency ( $\eta_{CS}$ ) calculated from fluorescence dynamics data of perovskite film and five different fullerene films coated perovskite layers.  $\eta_{CS} = k_p - k_0 / k_p$ , relevant parameters ( $\tau_{fl}$ ,  $k_p$ ,  $\tau_0$  and  $k_0$ ) are also shown.

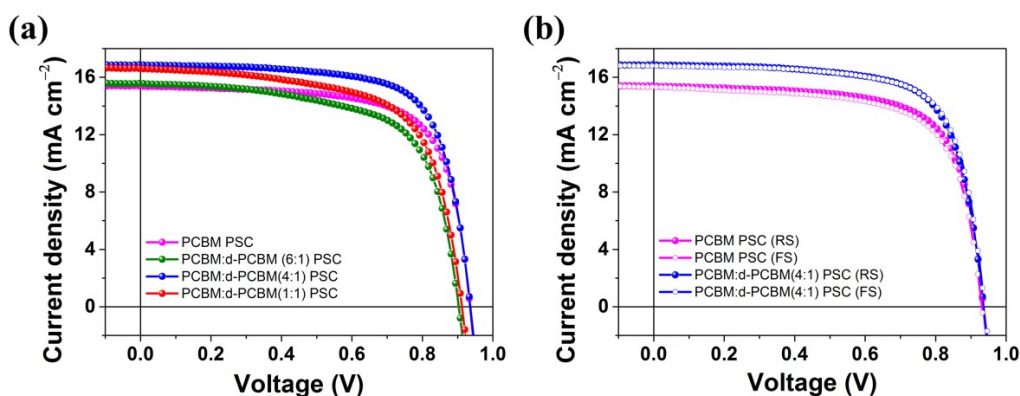
Film Samples	$\tau_{fl}$ (ns)	$k_p$ (ns <sup>-1</sup> )	$\tau_0$ (ns)	$k_0$ (ns <sup>-1</sup> )	$k_p - k_0$ (ns <sup>-1</sup> )	$\eta_{CS}$
PCBM film	1.146	0.872			0.708	0.684
PCBM:d-PCBM (6:1) film	0.885	1.130			0.966	0.747
PCBM:d-PCBM (4:1) film	0.737	1.356	6.101	0.164	1.190	0.784
PCBM:d-PCBM (1:1) film	1.465	0.682			0.518	0.613
d-PCBM film	1.627	0.615			0.451	0.579



**Figure S6** (a) UV-vis absorption spectra of PCBM film, PCBM:d-PCBM (4:1) film and d-PCBM film on quartz substrates. (b) UV-vis absorption spectra of perovskite film, perovskite/PCBM film, perovskite/PCBM:d-PCBM (6:1) film, perovskite/PCBM:d-PCBM (4:1) film, perovskite/PCBM:d-PCBM (1:1) film and perovskite/d-PCBM film.

**Table S4** Statistical  $J_{SC}$ ,  $V_{OC}$ , FF and PCE of four PSC devices from eight cells for every type, by reverse scan.

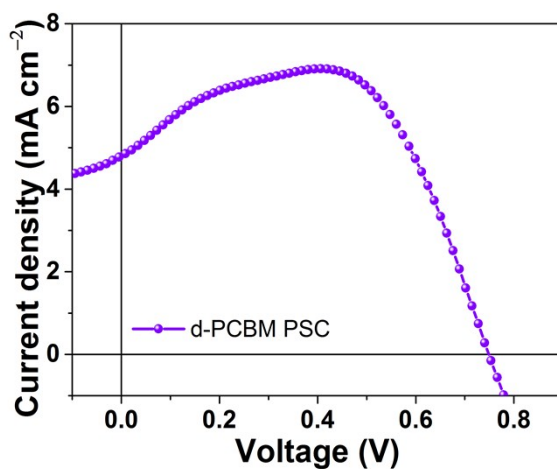
Solar Cells	$J_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (V)	FF	PCE (%)
PCBM PSC	15.68±0.19	0.911±0.040	0.72±0.02	10.34±0.26
PCBM:d-PCBM (6:1) PSC	15.90±0.24	0.937±0.045	0.70±0.01	10.57±0.31
PCBM:d-PCBM (4:1) PSC	16.70±0.32	0.941±0.021	0.73±0.01	11.43±0.24
PCBM:d-PCBM (1:1) PSC	16.32±0.20	0.926±0.011	0.63±0.02	9.46±0.32



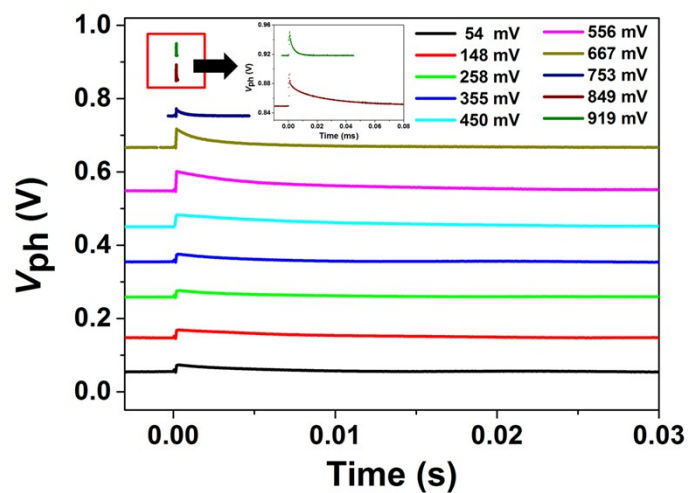
**Figure S7** (a)  $J$ - $V$  characteristic curves of four PSC devices based on PCBM, PCBM:d-PCBM (6:1), PCBM:d-PCBM (4:1) and PCBM:d-PCBM (1:1) by reverse scan. (b)  $J$ - $V$  characteristic curves of PCBM PSC and PCBM:d-PCBM (4:1) PSC by reverse scan and forward scan.

**Table S5**  $J_{SC}$ ,  $V_{OC}$ , FF and PCE of four PSC devices with the PCEs approaching to the statistical average data, by reverse scan.

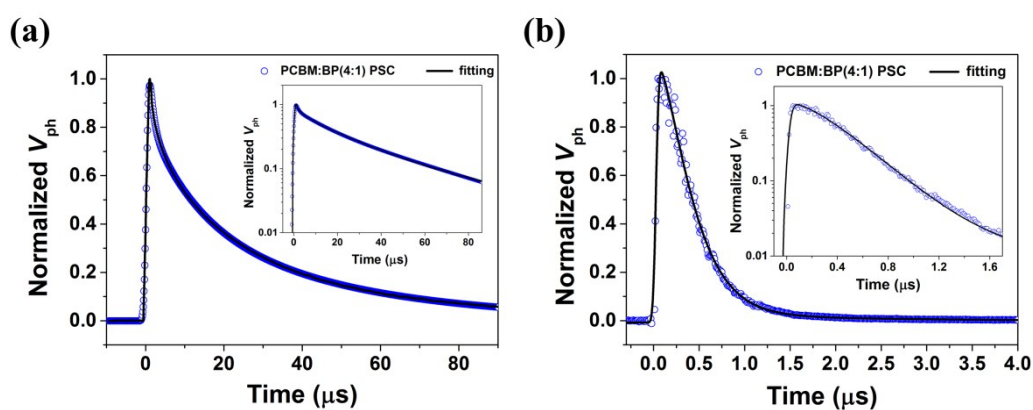
Solar Cells	$J_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (V)	FF	PCE (%)
PCBM PSC	15.49	0.93	0.70	10.11
PCBM:d-PCBM (6:1) PSC	15.68	0.92	0.72	10.39
PCBM:d-PCBM (4:1) PSC	16.83	0.92	0.74	11.50
PCBM:d-PCBM (1:1) PSC	16.37	0.93	0.64	9.70



**Figure S8**  $J$ - $V$  characteristic curve of pure d-PCBM based PSC by reverse scan.



**Figure S9** TPV decay traces at diverse photo-induced voltage for PCBM:d-PCBM (4:1) PSC.



**Figure S10** (a) Exponential fitting example of TPV decay trace with a steady photovoltage of 850 mV for PCBM:d-PCBM (4:1) PSC. The inset shows the semi-logarithmic scale decay trace. (b) The corresponding photocurrent traces at the same illumination as TPV measurement at 850 mV at the linear and semi-logarithmic scale. The decay trace is also fitted by exponential function.