

# Single enantiomer chiral fullerenes enable interfacial toughening of perovskite solar cells

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## Experimental Section

**Materials:** MAcI (99.99%) and FAI (99.99%) were purchased from Greatcell Solar. PbI<sub>2</sub> was purchased from TCI. DMF (>99.8%), DMSO (>99.8%), chlorobenzene (>99.8%), 1,3-dichlorobenzene (>99.8%) and diethyl ether (>99.8%) were purchased from Acros Organics. PTAA was purchased from Xi'an Polymer Light Technology. All chemicals were used as received without further purification. Solar cell substrates are pre-patterned ITO glass obtained from Yingkou Advanced Election Technology Co., Ltd.

**Synthesis:** The bis[60]PCBM isomeric mixture was synthesized with three main steps, followed with isomer purification via peak-recycling HPLC LC-908, according to our previous work<sup>[1,2]</sup>. The pure racemate (>99.9%) of a given material underwent further chiral purification using a Chiralpak IE column into pure enantiomers (*anti-S*) 16,17-bis[60]PCBM (*eB*) (>99.9%) and (*anti-R*) 16,17-bis[60]PCBM (*eA*) (>99.9%) used in this work. Similar purification method was applied to isolate pure enantiomers (*S,R*, *f,sC*) 49,59-bis[60]PCBM (*tran-2A*) (>99.9%) and (*R,S*, *f,sA*) 49,59-bis[60]PCBM (*tran-2B*) (>99.9%), Figure 1B in the main context. The details of enantiomeric purification method can be found in our previous work<sup>[3]</sup>.

**Solar cell fabrication:** ITO glass was cleaned by sequentially washing with detergent, acetone and IPA, each step for 15 min and dried by nitrogen gas. Before use, the ITO was treated with UV

ozone for 30 min. PTAA (2 mg/mL in toluene) was spin-coated onto the cleaned ITO at 4000 rpm for 30 s, following with annealing at 100 °C for 10 min. The substrates were cooled down to room temperature before use. 1.4 M perovskite precursor solutions were constructed by mixing FAI, PbI<sub>2</sub>, and 30 mol% MACl in mixed solvents of DMF and DMSO (v/v = 9:1). 50 μL of the prepared precursor solution was spin-coated at 1000 rpm for 10 s and 5000 rpm for 30 s onto the PTAA-coated ITO substrate, 200 μL CB as anti-solvent was dripped on the film at 5 s before the end of the last procedure and then annealed at 150°C for 15 min. After deposition of the perovskite active layer, 50 μL of the fullerene ETL (5 mg/mL in DCB) solution was spin-coated on to the film at 2000 rpm for 45 s and annealed at 100°C for 1 min. Finally, 5 nm BCP and 100 nm copper was evaporated sequentially.

*Module fabrication:* P1 line was laser-scribed on the ITO substrates. The substrates were cleaned by sequentially washing with detergent, acetone and IPA, each step for 15 min and dried by nitrogen gas. Before use, the ITO was treated with UV ozone for 30 min. After that, a PTAA layer was blade-coated onto ITO glass substrates at a speed of 15 mm/s. The gap between blade coater and ITO substrates was 100 μm. PTAA solution was prepared by dissolving PTAA in toluene with a concentration of 2 mg/mL. 1.3 M FAPbI<sub>3</sub> and 0.4 M MACl were dissolved in mixed solvent of DMF and NMP (volume ratio = 1:1). Subsequently, the precursor solution was blade-coated onto the PTAA-covered ITO glass substrates with a gap of 300 μm at a movement speed of 15 mm/s. The nitrogen knife was applied during blade coating. After that, the perovskite films were annealed at 150°C for 15 min in 35% R.H. air. Then, bis-PCBM (2 mg/mL in CB) solution was blade-coated at a speed of 10 mm/s. with the gap of 500 μm. 5 nm BCP were thermally evaporated. The deposited layers were laser-scribed for P2 line and then 100 nm copper were thermally evaporated as electrode. A customer designed shallow mask was applied to define the P3 line.

*Characterization:* UV-Vis absorption and CD spectra of the enantiomers and racemate in toluene were recorded with Agilent Cary 5000 UV-Vis spectrophotometer and JASCO J-810 CD with scanning rate 200 nm/min. The HOMO and LUMO of molecular geometries were simulated using DFT, at the B3LYP/6-311G(2df, 2pd) level of theory. The *J-V* characteristics of solar cells were obtained using a Keithley 2400 source meter under simulated 1-sun AM 1.5G illumination (100 mW cm<sup>-2</sup>) with a solar simulator (Enlitech, SS-F5-3A) and the light intensity was calibrated by a Si photodiode. The *J-V* measurements were carried out in ambient air. The devices were measured

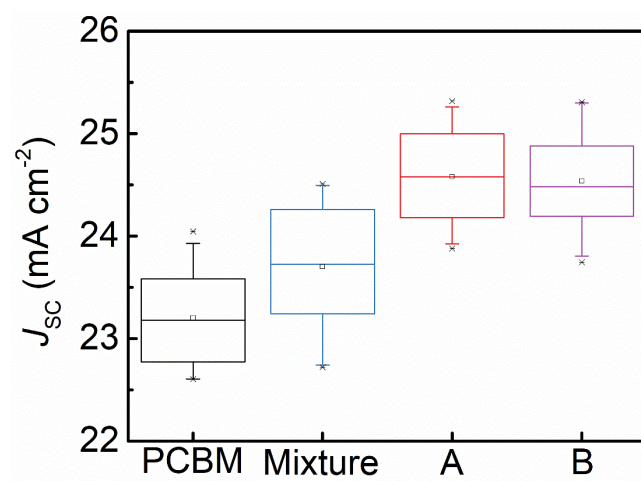
both in reverse scan (from 1.3 to -0.2 V, step 0.01 V) and forward scan (from -0.2 V to 1.3 V, step 0.01 V). The EQE was measured using an Enlitech EQE measurement system (QE-R3018).

*Encapsulation and stability measurements:* Devices were encapsulated in a nitrogen glovebox. PMMA (20 mg/mL in toluene) was first coated on the surface of cells. Then, Cytop was blade-coated atop PMMA. Finally, the device stacks were encapsulated using a cover glass with a UV-curable epoxy (Epoxy Technology, OG159-2) applied along its perimeter. A piece of black tape was attached to the exterior of the cover glass to protect the solar cell during UV curing. The operational stability tests were carried out at the MPPT for the encapsulated devices under AM1.5 illumination (100 mW/cm<sup>2</sup>) in ambient air at 40 °C or 85 °C. The voltage at the MPPT was automatically applied, and the power output of the devices was tracked.

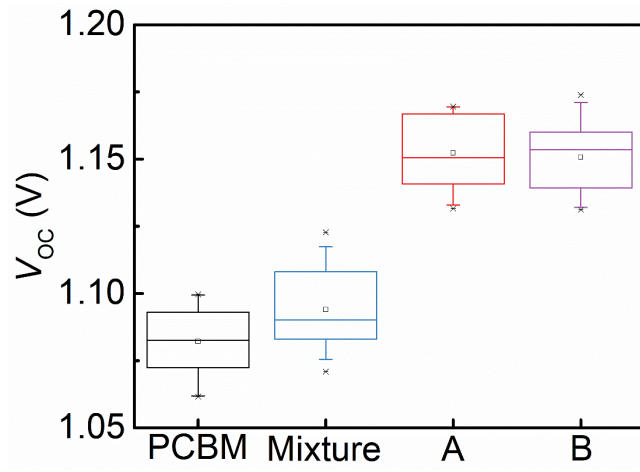
*Computational method:* All the spin-polarized DFT calculations are performed by the Vienna Ab initio Simulation Package (VASP) [4] with the projector augmented wave (PAW) method [5]. The exchange-functional is treated using the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) [6] functional. The energy cutoff for the plane wave basis expansion was set to 400 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.2 eV. The gamma point sampling was used in the Brillouin zone for all surface structure optimization. The self-consistent calculations apply a convergence energy threshold of 10<sup>-4</sup> eV, and the force convergency was set to 0.05 eV/Å. The bulk structure of FAPbI<sub>3</sub> was optimized using the k-point of 4×4×4, and the FAPbI<sub>3</sub> (100) surfaces was built with 36 Pb, 36 C, and 108 I atoms. The adsorption energy of *eA* and *trans-2A* were calculated following:

$$E_{\text{ad}} = E_{\text{surf+ad}} - E_{\text{surf}} - E_{\text{ad-ref}}$$

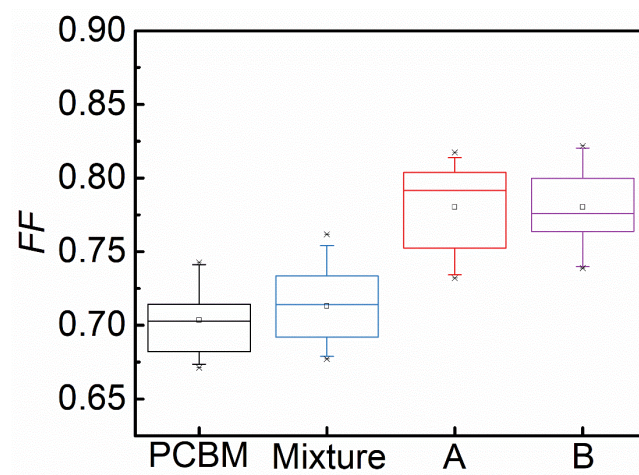
Where  $E_{\text{surf+ad}}$ ,  $E_{\text{surf}}$ , and  $E_{\text{ad-ref}}$  refer to the energy of *eA* / *trans-2A* adsorbed on the surface, bare surface, and *eA* / *trans-2A* itself, respectively.



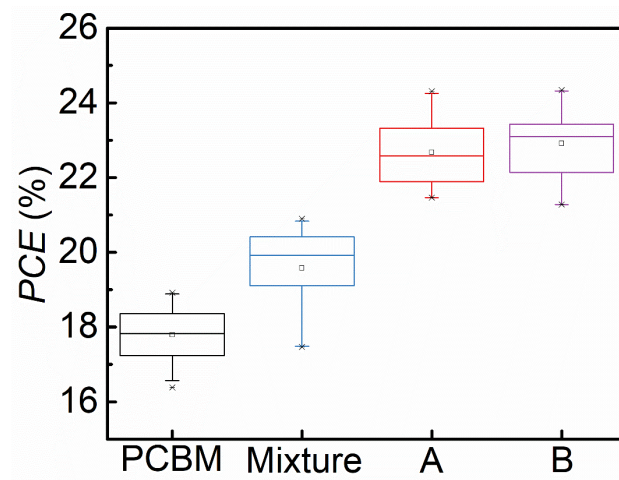
**Fig. S1**  $J_{SC}$  distribution of different solar cells. 20 devices were fabricated and studied in each condition.



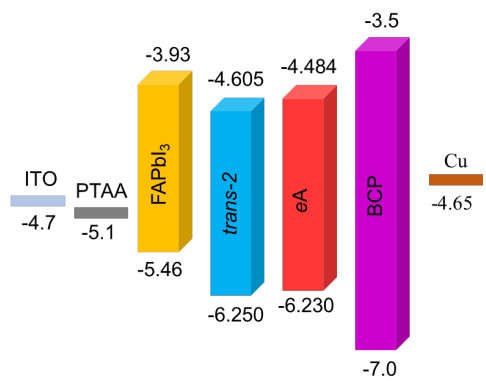
**Fig. S2**  $V_{oc}$  distribution of different solar cells. 20 devices were fabricated and studied in each condition.



**Fig. S3** *FF* distribution of different solar cells. 20 devices were fabricated and studied in each condition.

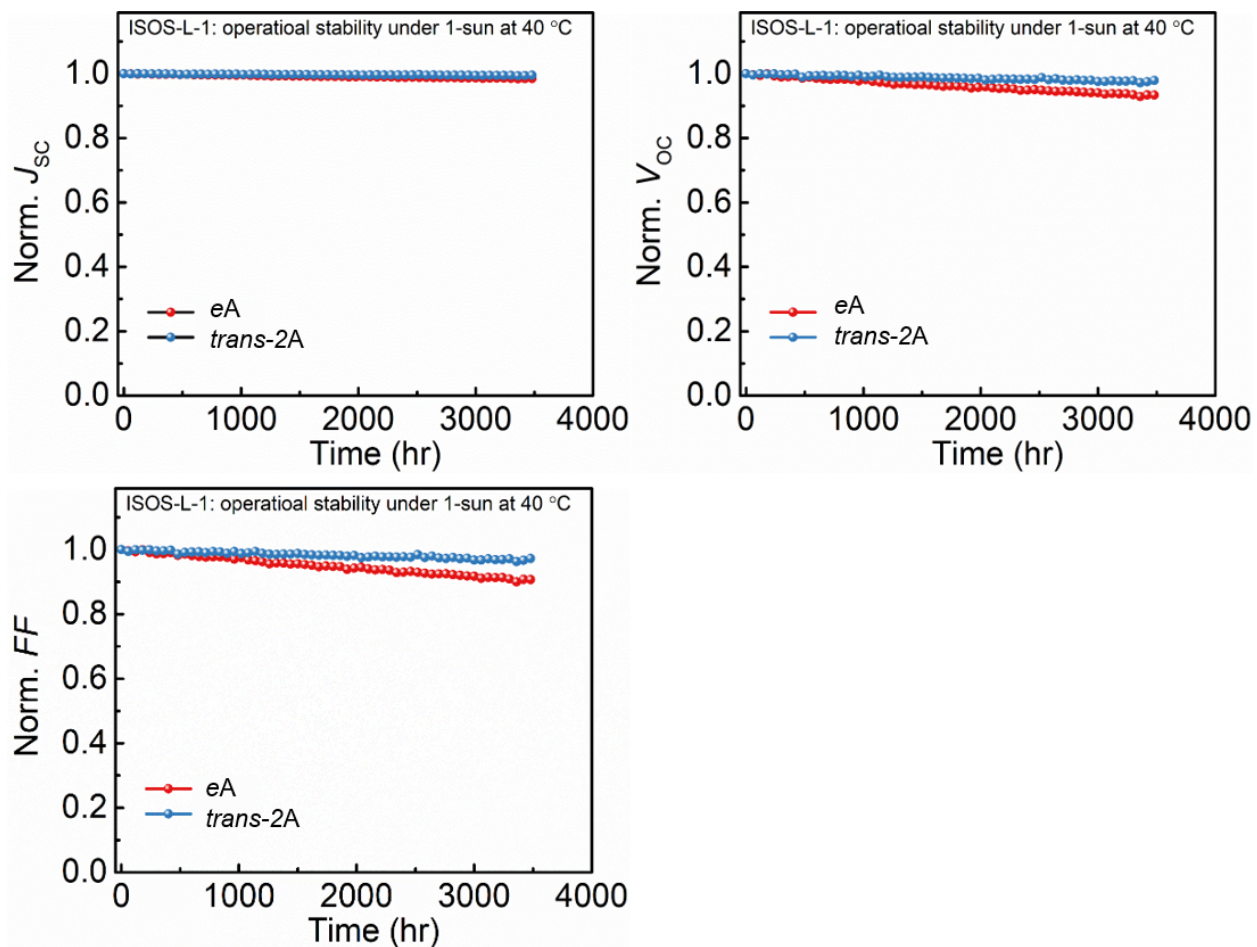


**Fig. S4** PCE distribution of different solar cells. 20 devices were fabricated and studied in each condition.

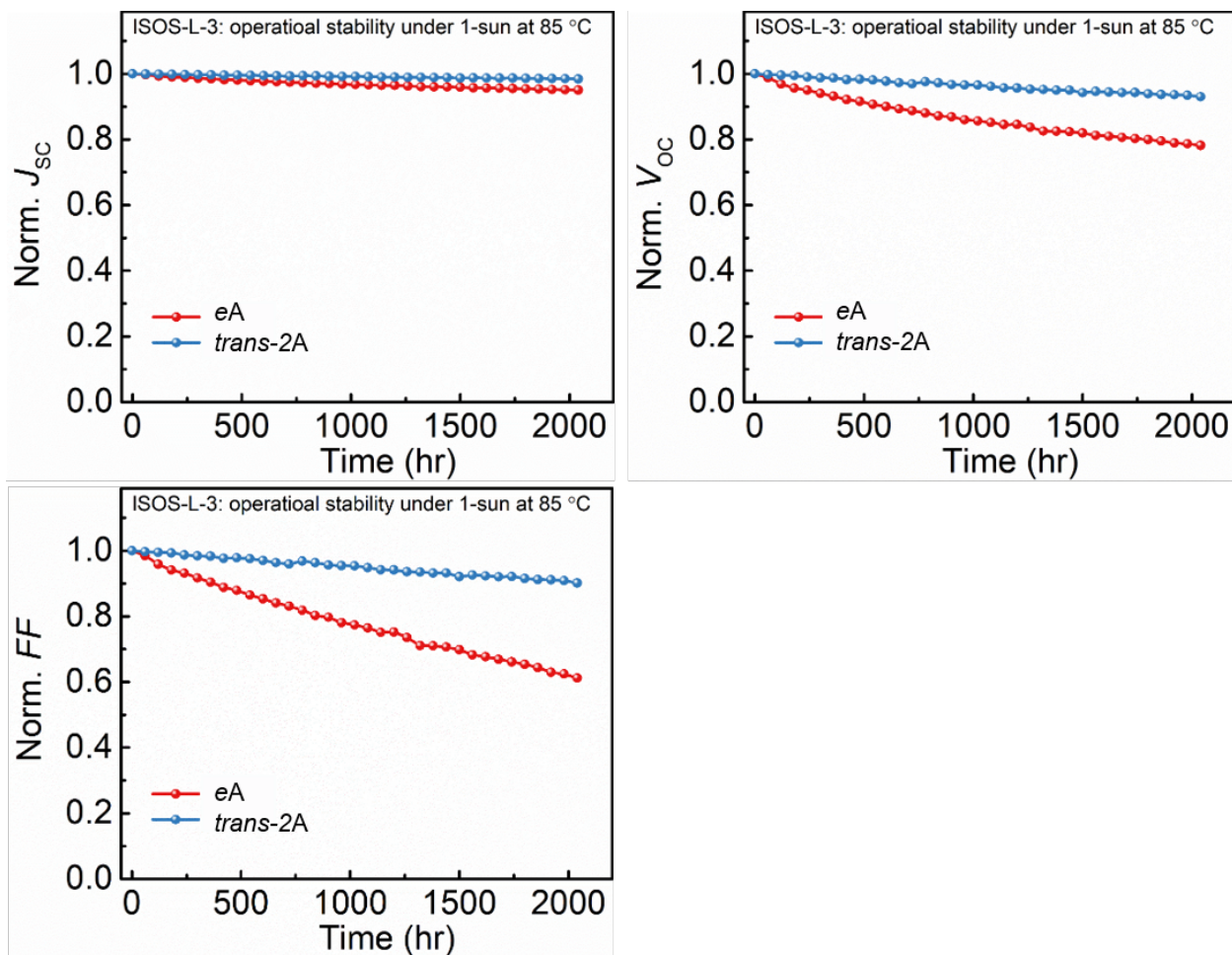


**Fig. S5.** The corresponding energy level diagram of PSC.

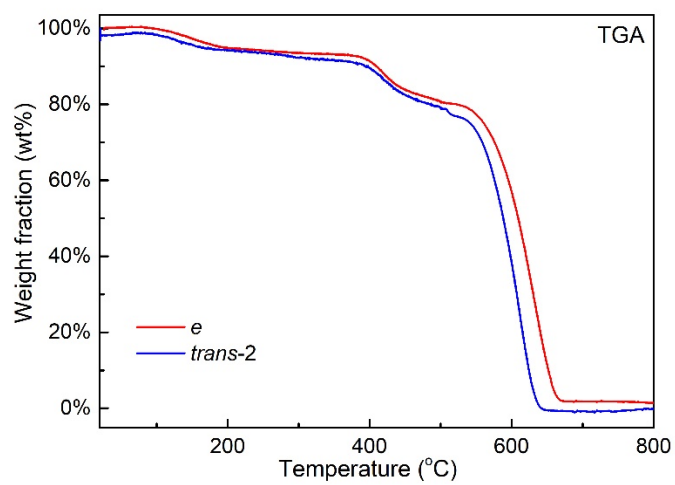




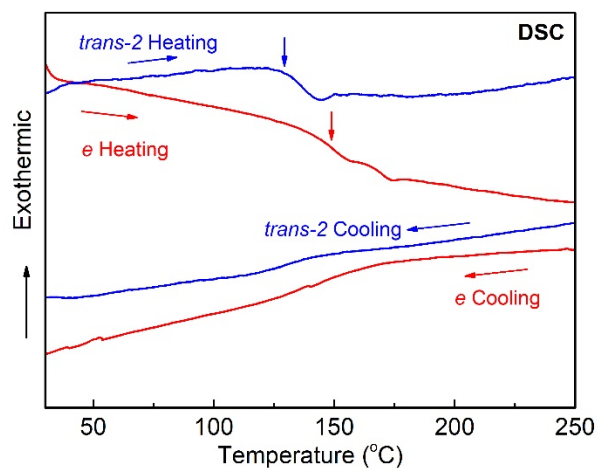
**Fig. S6** Normalized  $J_{sc}$ ,  $V_{oc}$  and  $FF$  as a function of time for encapsulated PSCs under simulated 1-sun illumination in 40 °C ambient air.



**Fig. S7** Normalized  $J_{sc}$ ,  $V_{oc}$  and  $FF$  as a function of time for encapsulated PSCs under simulated 1-sun illumination in 85 °C ambient air.



**Fig. S8** The TGA thermograms of *tran-2* and *e* bis[60]PCBM, All measurements were carried out in a N<sub>2</sub> atmosphere.<sup>[7]</sup>



**Fig. S9** The DSC thermograms of *tran-2* and *e* bis[60]PCBM.<sup>[7]</sup>

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