Raising the LUMO level of fullerene derivatives alleviates the output voltage loss in tin halide perovskite solar cells

Cheng Wu,[a] Weike Zhu,[a] Shurong Wang,[a] Zhiyuan Cao,[a] Liming Ding[b], Feng Hao[a]*

[a] *School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 611731, China. E-mail: haofeng@uestc.edu.cn*

[b] *Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China*

Synthesis method

Chemicals: All of the solvents and chemicals were used as received unless specially stated.
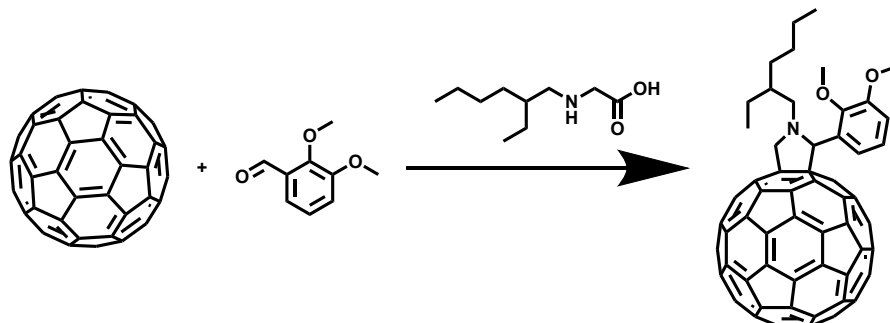
C$_{60}$-MP synthesis: C$_{60}$ (0.432 g, 0.6 mmol) and 2 eq. of (2-ethylhexyl)glycine, 1 eq. of 2,3-dimethoxybenzaldehyde were dissolved in 60 mL of 1,2-dichlorobenzene (1,2-DCB). The mixture was heated at 120 °C for 2 h with intense stirring. After cooled down, the organic layer was collected and evaporated under reduced pressure. The crude product was purified through column chromatography (petroleum ether/ethyl acetate = 3/1 vol/vol) to obtain C60-MP (0.188 g; yield: 31.1%) as a brown solid. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.65 -7.58 (m, 1H), 7.13 (t, J = 8.1 Hz, 1H), 6.86 (dt, J = 8.2, 1.7 Hz, 1H), 5.60 (d, J = 5.4 Hz, 1H), 5.06 (dd, J = 9.3, 3.8 Hz, 1H), 4.06 (dd, J = 9.3, 5.8 Hz, 1H), 3.87 (d, J = 8.6 Hz, 6H), 2.89 (td, J = 11.4, 3.0 Hz, 1H), 2.44 (td, J = 11.8, 3.2 Hz, 1H), 2.04 -1.91 (m, 2H), 1.62 -1.40 (m, 7H), 1.03 - 0.85 (m, 6H). HR-MS: (ESI) m/z: C$_{78}$H$_{29}$NO$_2$; calculate: 1011.2198; found: 1011.2182.
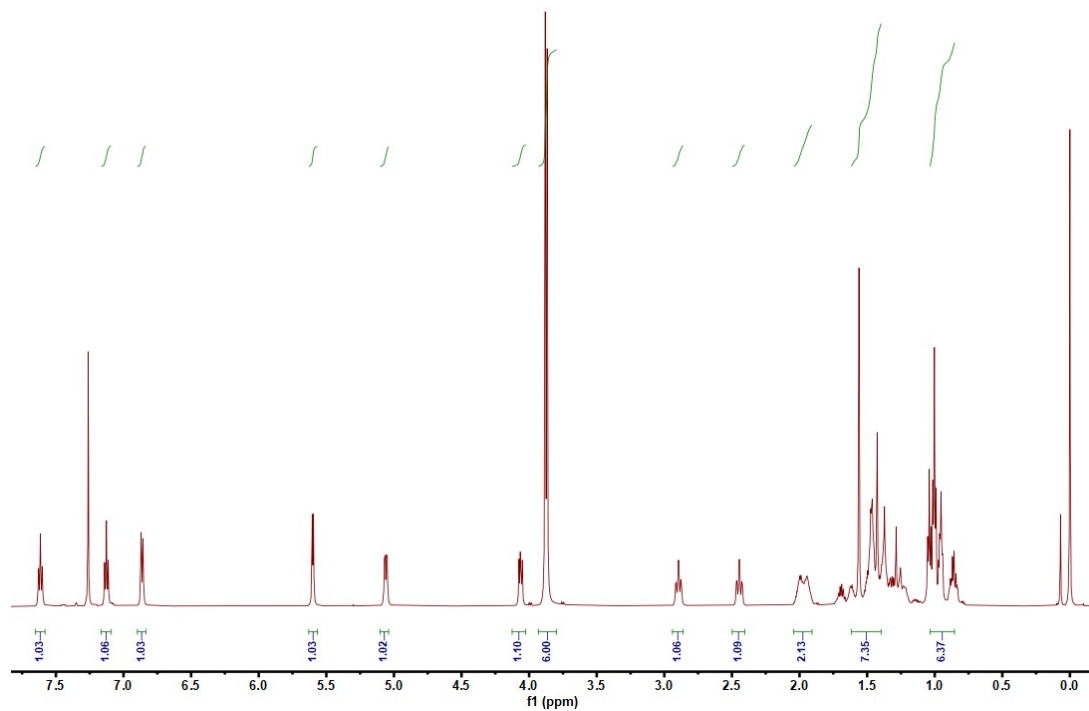
Fig. S1. ^{1}H-NMR spectrum of **C$_{60}$-MP** recorded in chloroform.
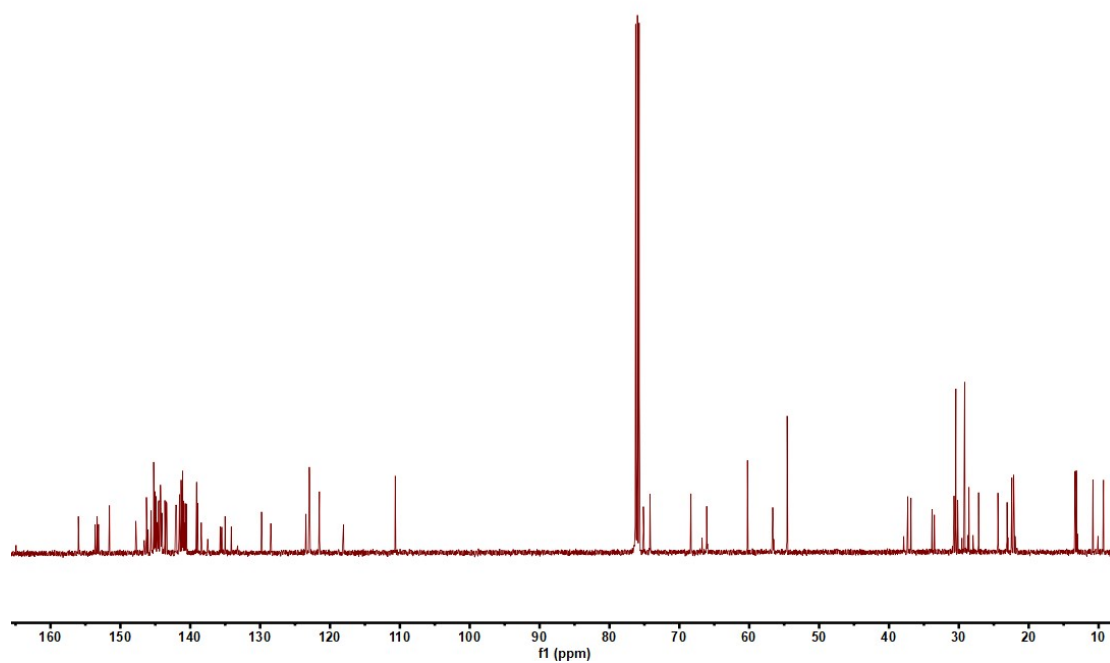
Fig. S2. ^{13}C-NMR spectrum of **C$_{60}$-MP** recorded in chloroform.

Fig. S3. HR-MS of **C₆₀-MP**.
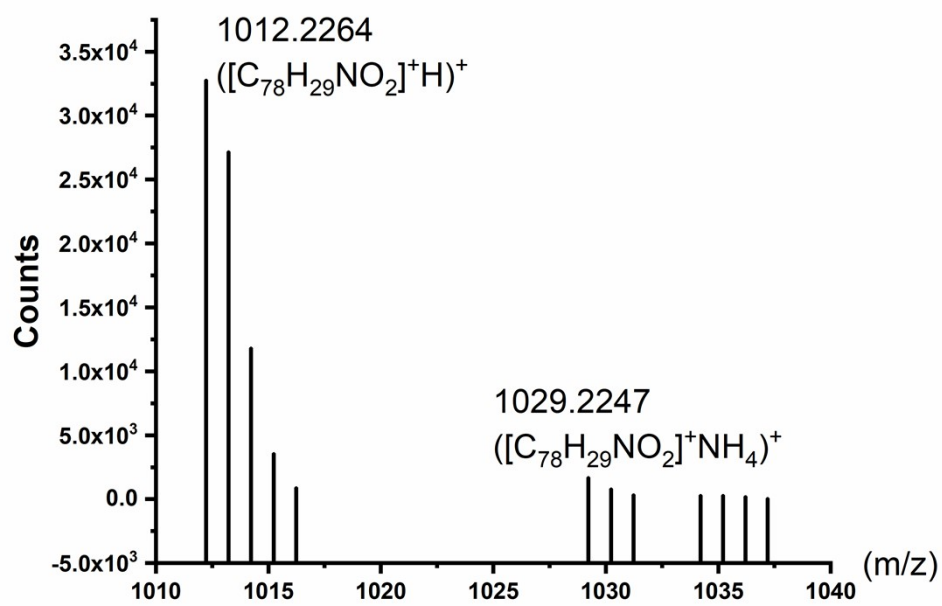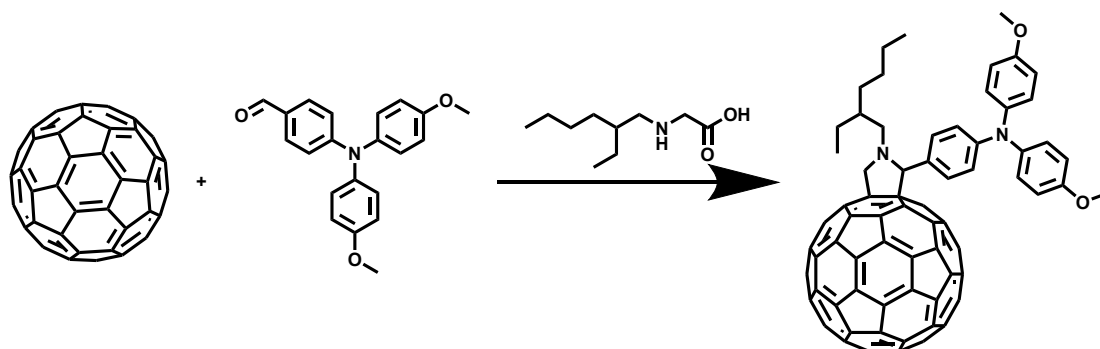
C$_{60}$-ETPA synthesis: C$_{60}$ (0.366 g, 0.5 mmol) and 2 eq. of (2-ethylhexyl)glycine, 1 eq. of 4-(bis(4-methoxyphenyl)amino)benzaldehyde were dissolved in 60 mL of 1,2-DCB. The mixture was heated at 120 °C for 2 h with intense stirring. After cooled down and the solution was removed by rotary evaporator under reduced pressure. The crude product was purified through column chromatography (petroleum ether/ethyl acetate = 9/1 vol/vol) to obtain C$_{60}$-ETPA (0.174 g; yield: 29.5%) as a brown solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.74 -7.03 (m, 6H), 6.96 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.5 Hz, 4H), 5.14 - 4.90 (m, 2H), 4.06 (d, J = 9.4 Hz, 1H), 3.80 (s, 6H), 3.10 (t, J = 11.5 Hz, 1H), 2.52 (t, J = 9.9 Hz, 1H), 2.20 - 1.89 (m, 2H), 1.46 (s, 6H), 1.13 - 0.98 (m, 6H). HR-MS: (ESI) m/z: C$_{90}$H$_{38}$N$_2$O$_2$; calculate: 1178.2766; found: 1178.2933.
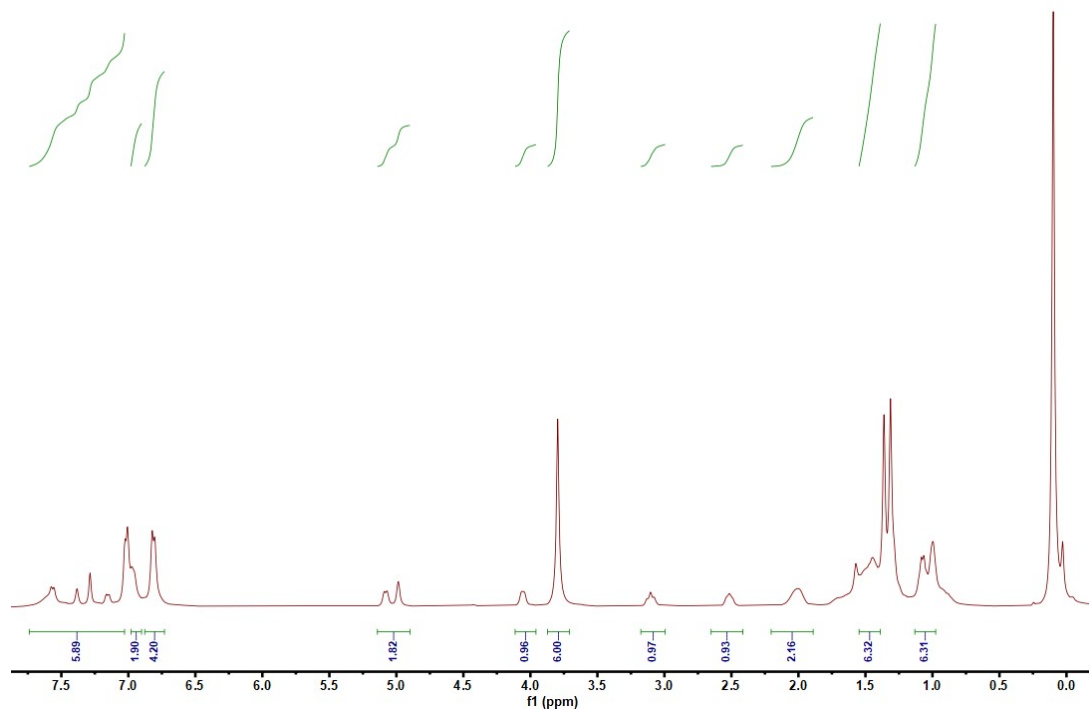
Fig. S4. ^{1}H-NMR spectrum of **C$_{60}$-ETPA** recorded in chloroform.
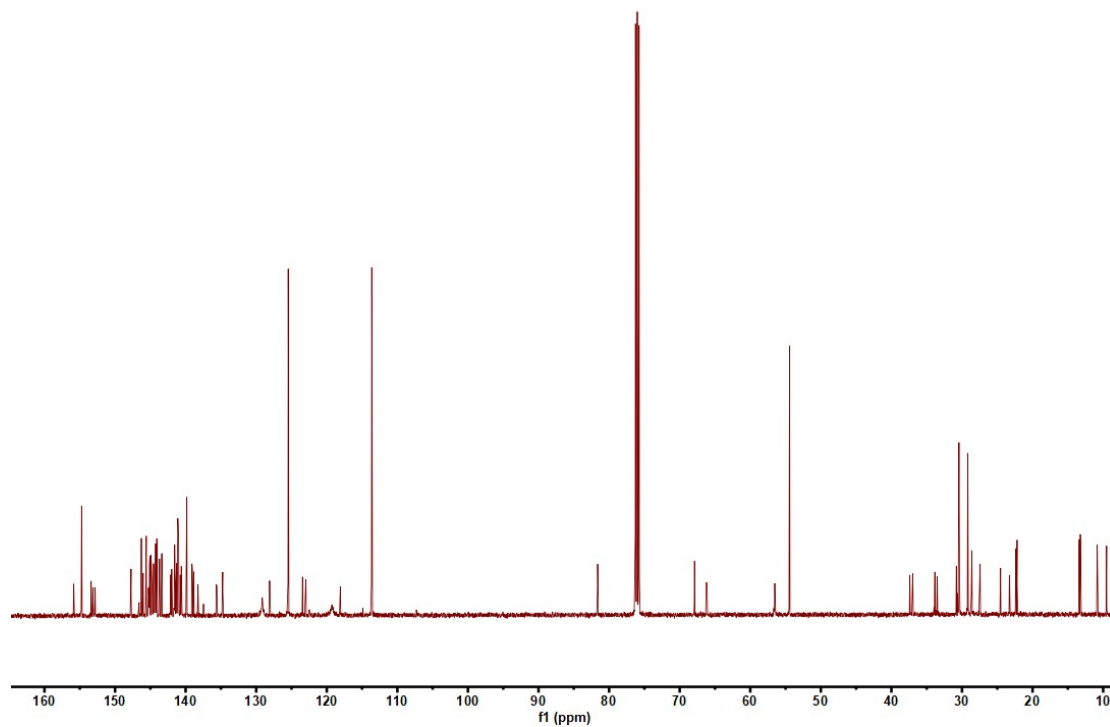
Fig. S5. ^{13}C-NMR spectrum of **C$_{60}$-ETPA** recorded in chloroform.
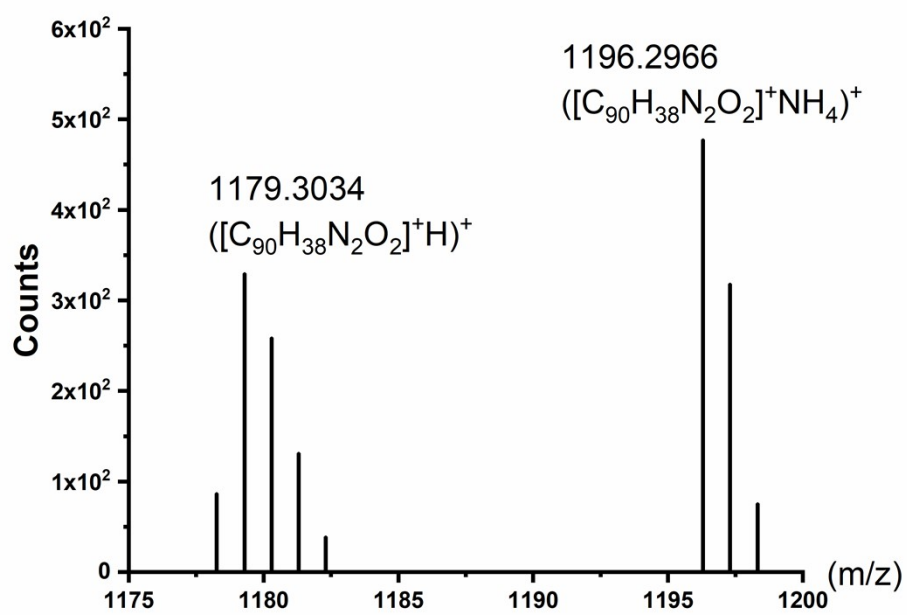
Fig. S6. HR-MS of **C₆₀-ETPA**.

Device preparation

The substrates were washed by sonication in deionized water, acetone and ethanol for 20 mins, respectively. After that, the ITO substrates were exposed in UV ozone for 15 mins. The PEDOT:PSS solution was coated on ITO substrates at 4000 rpm for 50 s and annealed at 140 °C for 20 mins. After that, 1.00 M perovskite solution was prepared by mixing FAI, MABr, SnI_2, and SnF_2 in the molar concentrations of 0.75: 0.25: 1: 0.10 with 10 mol% 2-phenylethanamine iodide (PEAI). The solution volume ratio of DMF and DMSO is 4: 1. After stirring 12h, the perovskite precursor solution spread onto the substrate and spin-coated at 8000 rpm for 60s, 150 μL CB anti-solvent was injected onto the film in the last 48 s, and then annealed at 80 °C for 10 mins. After cooling down to room temperature, 55 μL C_{60}-MP and C_{60}-ETPA solution (20 mg mL^{-1} in Chlorobenzene) was deposited on the perovskite film by spin-coated at 2000 rpm for 30s. Then, a BCP solution (0.5 mg mL^{-1} in IPA) was spin-coated at 4000 rpm for 30 s and annealed at 70 °C for 10 mins. Finally, 100 nm Ag electrode was deposited under a high vacuum system ($< 4 \times 10^{-6}$ Pa).

Measurement

UV-vis absorption spectra were measured by UV-2600 (Shimadzu). Cyclic voltammetry (CV) was tested in $CHCl_3$ with 0.1 M $TBAPF_6$ with a CHI-660E electrochemical workstation. The tested values were calculated according to the formula of $E_{LUMO} = -e(E_{red}^{onset} + 4.8)$. Photocurrent-voltage (*J-V*) curves were measured by a Keithley 2400 source-measure unit under standard AM 1.5G (100 mW cm^{-2}) illumination using a sunlight simulator (San-EI Electric) in the air. All the devices were masked with an aperture area of 0.096 cm^2. EQE spectra were measured by the quantum efficiency testing and analysis system QE-R (Enlitech). The steady photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectroscopy were measured by using fluorescence lifetime and steady state spectrometer Fluo Time 300 (PicoQuant) with a excitation wavelength at 465 nm laser. The Photo-CELIV, impedance spectroscopy, transient photovoltage (TPV) and Mott-Schottky curve (M-S) information were detected by Piaos system (FLUXiM) with a light intensity of 60 mW

LED. Electron mobility (μ_e) was measured by the Photo-CELIV, the data was calculated by the following equation:

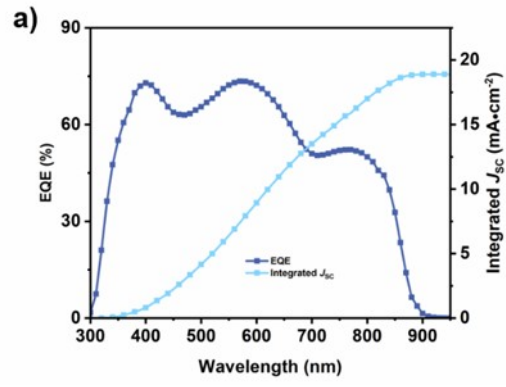$$\mu_e = \frac{2d^2}{3At_{max}^2[1 + 0.36 \, \triangle j/j(0)]} \quad \text{if } \triangle j < j(0) \tag{1}$$

Fig. S7. EQE spectrum of **PC₆₁BM** based device.
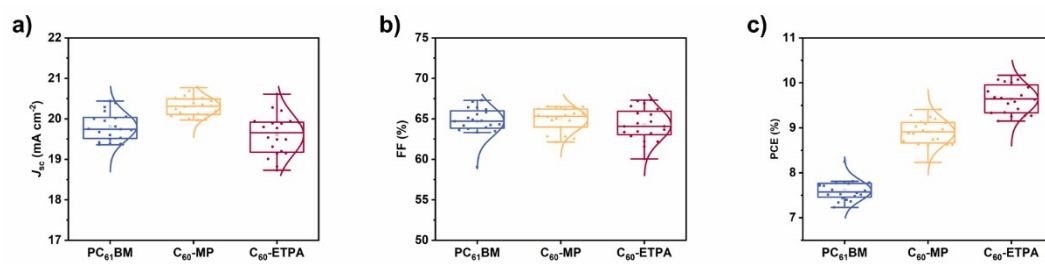
Fig. S8. Statistic data of J_{sc}(a), FF (b) and PCE (c) with ETMs **C$_{60}$-MP**, **C$_{60}$-ETPA** and PC$_{61}$BM.
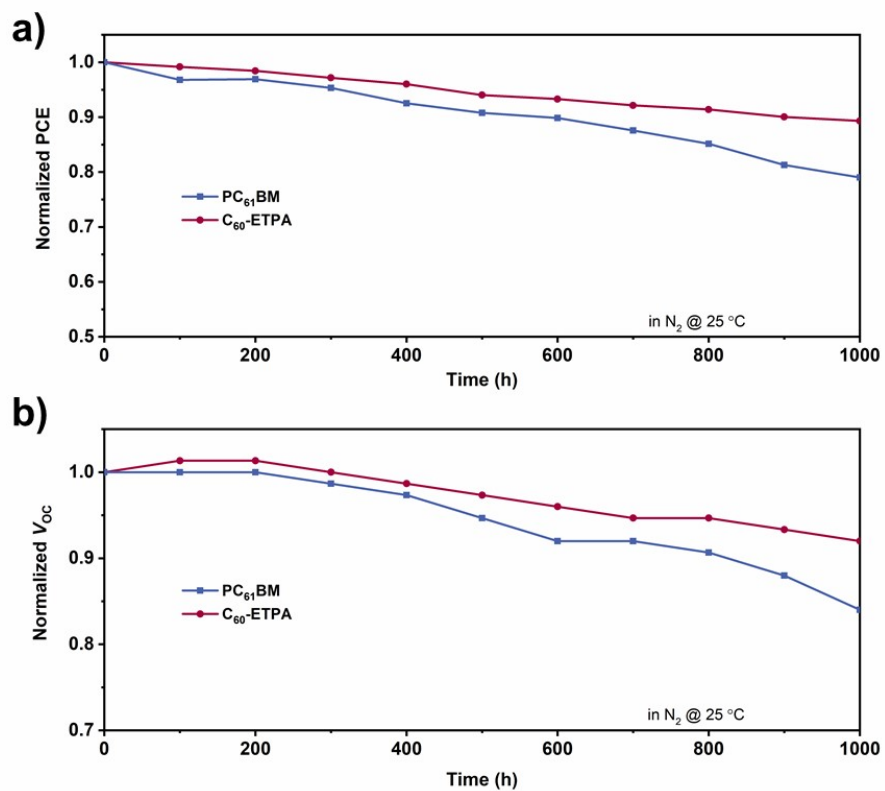
Fig. S9. Stability data of $PC_{61}BM$ and **C_{60}-ETPA** based PSCs in N_2 condition, (a) Normalized PCE, (b) Normalized V_{oc}.
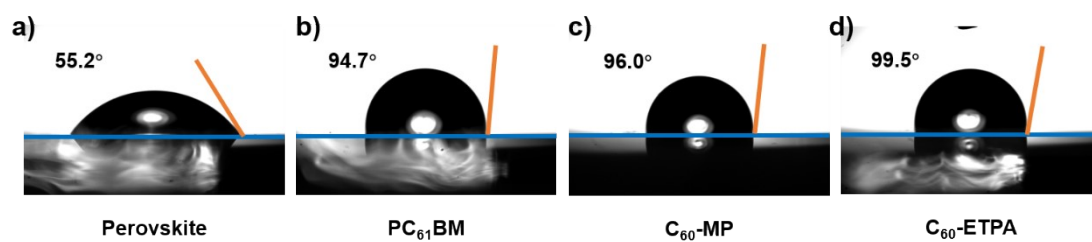
Fig. S10. water contact angle of perovskite (a), PC$_{61}$BM (b), **C$_{60}$-MP** (c) and **C$_{60}$-ETPA** (d) film.

Table S1. The photoelectric and electrochemical properties of C_{60}-MP, C_{60}-ETPA and $PC_{61}BM$.

ETM	λ_{edge} (nm)	E_{0-0} (eV)	HOMO (eV)	LUMO (eV)	Electron mobility ($cm^2\ V^{-1}\ s^{-1}$)	Conductivity ($S\ cm^{-2}$)
$PC_{61}BM$	717	1.73	-5.85	-4.12	3.60×10^{-5}	5.17×10^{-6}
C_{60}-MP	740	1.68	-5.75	-4.07	5.23×10^{-5}	9.34×10^{-6}
C_{60}-ETPA	728	1.70	-5.74	-4.04	4.66×10^{-5}	7.93×10^{-6}

Table S2. The device performances of TPSCs with $PC_{61}BM$, C_{60}-MP and C_{60}-ETPA.

ETM	V_{oc}/V	J_{sc}/mA cm^{-2}	FF/%	PCE/%
$PC_{61}BM$	0.63	19.34	67.26	8.25
	(0.60 ± 0.03)	(19.90 ± 0.54)	(63.17 ± 4.13)	(7.59 ± 0.36)
C_{60}-MP	0.69	20.51	66.46	9.43
	(0.67 ± 0.03)	(20.31 ± 0.34)	(65.31 ± 3.18)	(8.91 ± 0.51)
C_{60}-ETPA	0.76	19.94	67.21	10.17
	(0.77 ± 0.02)	(19.67 ± 0.94)	(63.69 ± 3.63)	(9.66 ± 0.51)

ETM	τ_1 (ns)	A_1(%)	τ_2 (ns)	A_2 (%)	τ_{avg} (ns)
PVSK	5.40	63.12	11.44	36.88	8.74
PVSK /$PC_{61}BM$	1.85	42.09	4.77	57.91	4.13
PVSK /C_{60}-MP	1.48	97.31	2.95	2.69	1.56
PVSK /C_{60}-ETPA	1.71	66.18	3.26	33.82	2.47

Table S3. Summary of TRPL parameters of different layers.