

Enhancing the Performance of Polymer Photovoltaic Cells by Using an Alcohol Soluble Fullerene Derivative as the Interfacial Layer

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EXPERIMENTAL PART

Materials and Instruments. Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. Compound **1** was synthesized according to the literature procedure.⁴⁸ Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium with benzophenone as an indicator under nitrogen atmosphere. Hexane and dichloromethane (DCM) were distilled from CaH₂. Chloroform was distilled before use. Unless otherwise noted, all reactions were performed under an atmosphere of nitrogen and monitored by thin layer

chromatography (TLC) on silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200-300 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. The thickness of the blend films was determined by a Dektak 6 M surface profilometer. The electrochemical behavior of the materials was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrafluoroborate solution in CH_3CN :1,2-dichlorobenzene (DCB) or CH_3CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/S. A Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO_3 (0.01 M in CH_3CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (F_c) redox system and assumption that the energy level of F_c is 4.8 eV below vacuum.

Polymer Solar Cell Fabrication and Characterization. Polymer solar cells (PSCs) were fabricated with the device configuration of ITO/PEDOT:PSS/polymer:PC₇₁BM/Al or ITO/PEDOT:PSS/Polymer:PC₇₁BM/interfacial layer/Al. The conductivity of ITO was 20 Ω/\square . PEDOT:PSS is Baytron A1 4083 from H. C. Starck and was filtered with a 0.45 μm PVDF film before use. A thin layer of PEDOT:PSS was spin-coated on top of cleaned ITO substrate at a speed of 3000 rpm for 60 s and dried subsequently at 130 $^\circ\text{C}$ for 15 min on a hotplate before being transferred into a glove box. The

thickness of the PEDOT:PSS layer was about 40 nm. The blend of polymers and PC₇₁BM was dissolved in DCB and heated at 90 °C overnight to ensure a sufficient dissolution, and then spin-coated onto PEDOT:PSS layer. The **FN-C60** solution in methanol was spin-coated on the top of the obtained active layer at 2000 rpm for 30 s to form a thin interfacial layer of about 5 nm. Finally, 100 nm of aluminum was deposited onto the interfacial layer by thermo evaporation at a pressure of 10⁻⁴ Pa through a shadow mask. Five cells were fabricated on one substrate with an effective area of 0.04 cm². The measurement of devices was conducted in air without encapsulation. Current-voltage characteristics were recorded using an Agilent B2902A Source Meter and an AM 1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mWcm⁻² as the white light source. The light intensity was calibrated with a standard single-crystal Si photovoltaic cell. The temperature while measuring the J-V curves was approximately 25 °C.

Synthesis of Compounds

Synthesis of 9,9-bis(6-bromohexyl)-9H-fluorene-2-aldehyde (2). *n*-BuLi (2.5 M solution in *n*-hexane, 5.4 mL, 13.5 mmol) was added to a stirred solution of compound **1** (6.79 g, 11.9 mmol) in diethyl ether (160 mL) under nitrogen at -78 °C over 10 min, then the reaction mixture was allowed to warm to 0 °C gradually and stirred at this temperature for 4 h. The reaction mixture was cooled to -78 °C again; N,N-dimethylformamide (1.05 g, 14.4 mmol) was injected; and the reaction mixture was allowed to warm to room temperature gradually and stirred overnight. The reaction mixture was neutralized with aqueous HCl (2 M), water (150 mL) and diethyl

ether (150 mL) were added; the organic layer was separated; and the aqueous layer was extracted with diethyl ether (150 mL). The combined organic layers were washed with brine (50 mL), dried over Mg_2SO_4 , and evaporated to dryness. The residue was purified by flash column chromatography (SiO_2 , petroleum ether (60-90 °C):DCM = 4:1 by volume) to give **2** as a colorless solid (5.12 g, 83 %). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 9.95 (s, 1H), 7.70-7.80 (m, 4H), 7.34 (m, 3H), 3.19 (t, 4H), 1.97 (m, 4H), 1.58 (m, 4H), 1.10 (m, 4H), 0.99 (m, 4H), 0.51 (m, 4H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 192.3, 151.8, 151.2, 147.5, 139.6, 135.4, 130.7, 128.9, 127.3, 123.0, 122.9, 121.0, 120.0, 55.1, 40.0, 33.8, 32.6, 29.0, 27.7, 23.5. Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{Br}_2\text{O}$: C 60.01, H 6.20. Found: C 60.00, H 6.18.

Synthesis of FBr-C60. A mixture of 9,9-bis(6-bromohexyl)-9H-fluorene-2-aldehyde (2595 mg, 4.99 mmol), C_{60} (701 mg, 0.97 mmol), 2-(methylamino)acetic acid (182 mg, 2.05 mmol), and toluene (150 mL) was stirred and refluxed under nitrogen for 2 hours. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography (SiO_2 , petroleum ether 60-90 °C:toluene = 10:1 by volume) and high-pressure liquid chromatography (HPLC) (toluene as the eluent) to afford **FBr-C60** as a brown solid (140 mg, 11%). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.06-7.98 (br, 1H), 7.66-7.61 (m, 2H), 7.53-7.45 (br, 1H), 7.25-7.23 (m, 3 H), 5.05 (br, 2H), 4.30 (d, 1H), 3.21-3.13 (br, 4H), 2.86 (s, 1H), 1.93-1.88 (br, 4H), 1.60-1.50 (br, 4H), 1.19-0.81 (br, 8H), 0.63-0.25 (br, 4H). MADI-TOF MS: calcd 1265.1, found 1266.2 ($\text{M}+\text{H}$) $^+$.

Synthesis of FN-C60. A mixture of **FBr-C60** (41 mg, 0.032 mmol), THF (15 mL), and trimethylamine alcohol solution (30%, 5 mL) was stirred at room temperature for 48 h. Methanol (10 mL) was added to the mixture to dissolve the precipitate, and the reaction was stirred for another 24 h. After the removal of the solvent under reduced pressure, the residue was dissolved in methanol (3 mL) and precipitated into a large amount of acetone. The resulted precipitates were collected by filtration and washed with a large amount of acetone. The crude product was dissolved in a minimum amount of methanol and further precipitated into a large amount of diethyl ether. The formed precipitates were collected by filtration and dried under high vacuum to afford **FN-C60** (35 mg, 79%) as a dark solid. ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.89-7.34 (br, 7H), 4.00-3.80 (br, 3H), 3.1-2.8 (br, 23H), 1.45 (br, 4H), 1.05 (br, 8H). MADLI-TOF MS: calcd 1383.28, found 1368.8 (M-CH₃)⁺.

Table S1. The photovoltaic parameters of the devices based on bare Al cathode, FN-C60/Al cathode and LiF/Al cathode.

the active layer	interlayer	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	Eff (%)
P3/PC₇₁BM	no	0.79	7.73	0.57	3.50
	FN-C60	0.84	8.56	0.65	4.64
	CH ₃ OH	0.81	8.45	0.55	3.79
	LiF	0.82	8.32	0.63	4.30
HXS-1/PC₇₁BM	no	0.82	8.09	0.65	4.27
	FN-C60	0.86	8.74	0.70	5.25
	CH ₃ OH	0.84	8.48	0.66	4.70
	LiF	0.82	8.58	0.67	4.69

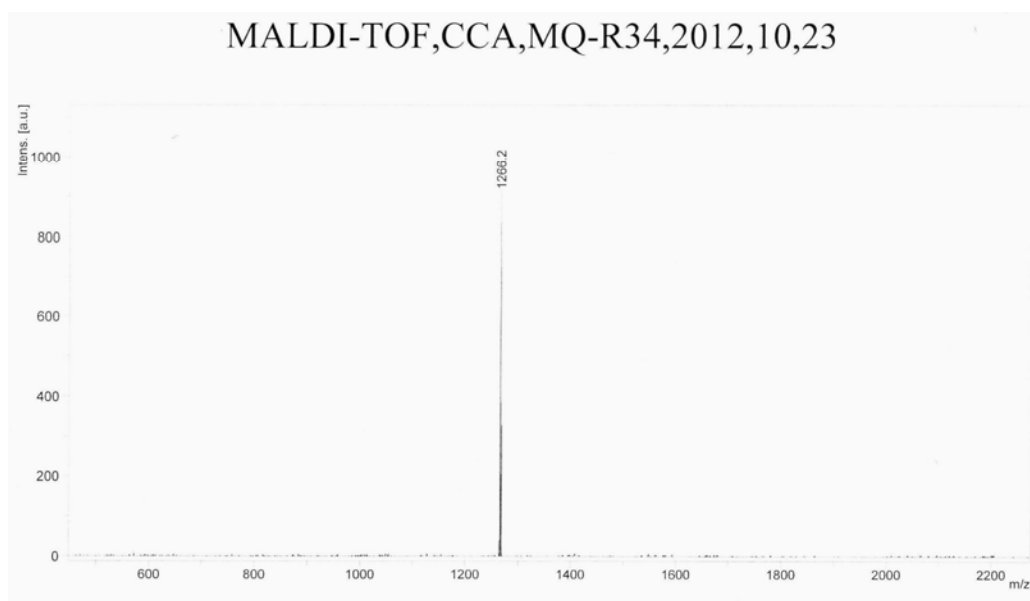


Figure S1 the MALDI-TOF spectra of FBr-C60

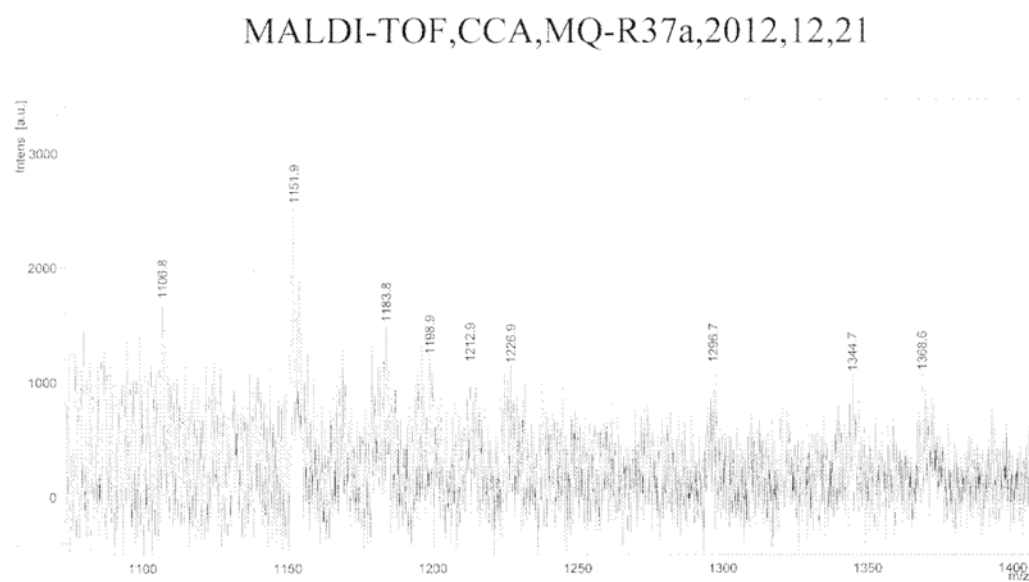


Figure S2 the MALDI-TOF spectra of FN-C60

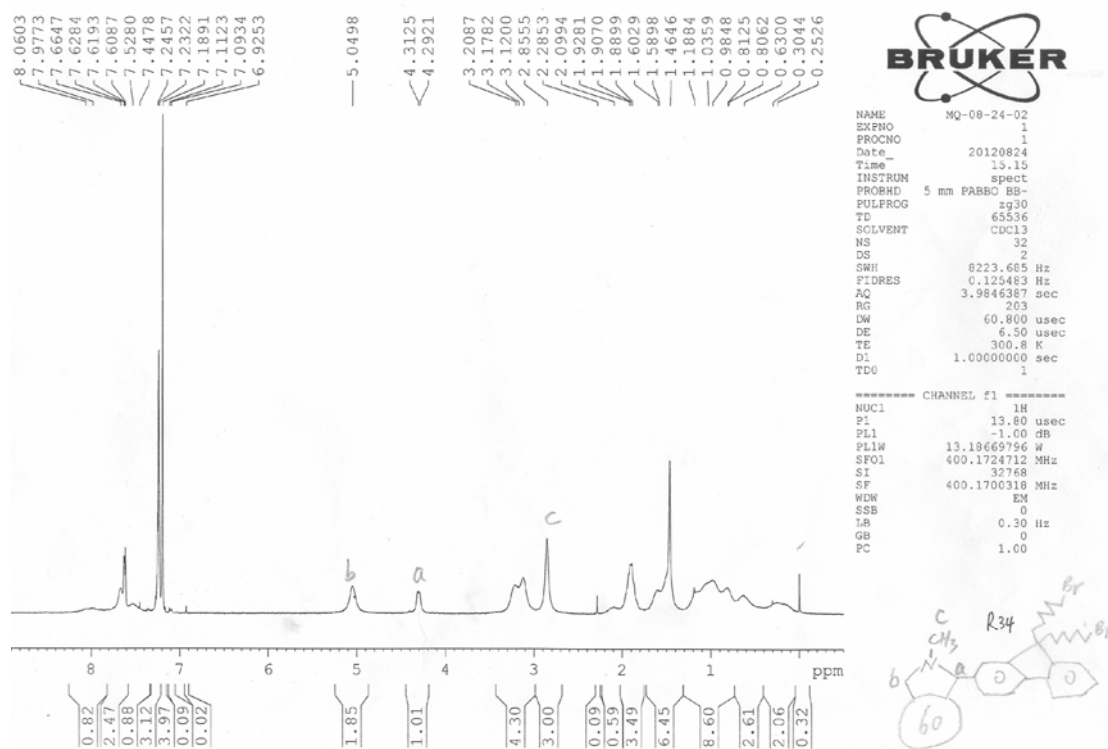


Figure S3 the ¹H NMR spectra of FBr-C60

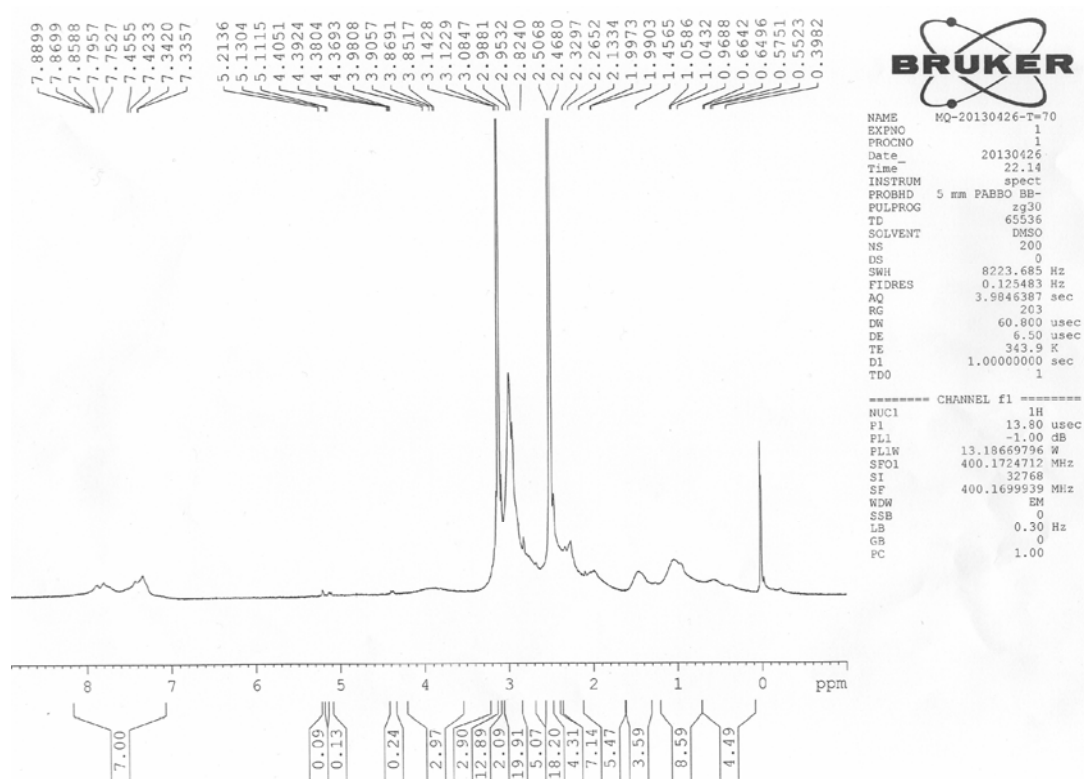


Figure S4 the ¹H NMR spectra of FN-C60