Ethanol-Processable, Highly Crystalline Conjugated Polymers for Eco-Friendly Fabrication of Organic Transistors and Solar Cells

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Methods

Scheme S1. Synthetic route to the ethanol-soluble donor and acceptor materials, PPDT2FBT-A and Bis-C$_{60}$-A. Reagents and reaction conditions: a) sodium *tert*-butoxide, ethanol, reflux, 48 h; b) Pd$_2$(dba)$_3$, tris(*o*-tolyl)phosphine, toluene; c) sarcosinic acid, chlorobenzene, N$_2$, reflux.

Synthesis: Fullerene (**C$_{60}$**) and 1,4-dibromo-2,5-dihydroxybenzene (**1**) were purchased from Solamer and Sigma-Aldrich and used without further purification. 1,3-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)propan-2-yl-toluenesulfonate (**2**) and 3,4,5-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzaldehyde (**4**) were prepared as previously described.[1-2] 1,4-Dibromo-2,5-bis(1,3-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)propan-2-yloxy)benzene (**M1**) was synthesized by following procedures. 1,4-Dibromo-2,5-dihydroxybenzene (**1**) (1.0 g, 3.8 mmol) was dissolved in ethanol (20 mL) and sodium *tert*-butoxide (0.77 g, 7.9 mmol)

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was added. The mixture was stirred at room temperature for 1 h under a N_2 atmosphere. Compound **2** (4.2 g, 7.9 mmol) was added dropwise and the reaction mixture was stirred for 48 h under reflux. After partial evaporation of the solvent, H_2O was added and the mixture was extracted with dichloromethane (CH_2Cl_2). The organic extracts were washed with 10% sodium hydroxide (NaOH) solution, dried over anhydrous magnesium sulfate ($MgSO_4$) and the solvent was evaporated to afford the crude product. After silica gel column chromatography (SiO_2, eluent ethyl acetate/methanol = 95/5, v/v), a colorless oily compound, **M1** (0.7 g, 60%), was obtained. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30 (s, 2H), 4.33 (m, 2H), 3.69 (m, 8H), 3.56 (m, 30H), 3.48 (m, 8H), 3.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.4, 121.8, 112.5, 80.6, 71.7, 70.5, 70.4, 70.3, 58.9.

OFET device fabrication and characterization: OEFTs were fabricated in a bottom-gate and top-contact configuration to characterize the electrical performance of PPDT2FBT-A using either CB or ethanol as the processing solvent. A highly *n*-doped (100) Si wafer (< 0.005 Ω cm) with a thermally grown 300 nm-thick SiO_2 layer (C_i = 10 nF cm^{-2}) was utilized as the gate and dielectric. The SiO_2/Si wafers were treated with an OTS self-assembled monolayer as previously reported.[3] The substrates were then washed sequentially with toluene, acetone, and isopropyl alcohol, and dried with nitrogen gas. PPDT2FBT-A was dissolved in ethanol or CB at ~2 mg mL^{-1} and stirred at 80 $^{\circ}$C for 5 h, filtered through a 0.2 μm membrane, and spin-coated at 3000 rpm for 50 s onto the OTS-treated SiO_2/Si substrate. Au electrodes (40 nm thick) were thermally evaporated through a shadow mask onto the semiconducting active layer. The electrical performance of the FETs was measured in a N_2-filled glovebox using a Keithley 4200 semiconductor parametric analyzer. The field-effect mobility was estimated in the saturation regime ($|V_{DS}| > |V_{GS}-V_T|$) using the following

equation:

$$I_{DS} = \mu \frac{W C_i}{2L} (V_{GS} - V_T)^2$$

where I_{DS} is the drain-to-source current, W and L are the semiconductor channel width and length, respectively, μ is the mobility, C_i is the capacitance per unit area of the dielectric, and V_{GS} and V_T are the gate and threshold voltage, respectively.

SCLC Measurements: Hole- and electron-only devices with pristine PPDT2FBT-A, Bis-C_{60}-A, and their blend films as the active layer were measured by the SCLC method using ITO/PEDOT:PSS/active layer/Au (hole-only) and ITO/ZnO/active layers/Ca/Al (electron-only) device structures, respectively. The films were prepared as described in the device fabrication section. A range of 0-8 V was used for the current-voltage measurement, and the results were fitted to the Mott-Gurney equation:

$$J_{SCLC} = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{L^3}$$

where ε_0 is the permittivity of free space (8.85×10^{-14} F cm^{-1}), ε is the relative dielectric constant of the active layer, μ is the charge carrier mobility, V is the potential across the device ($V = V_{applied} - V_{bi} - V_{series}$) corrected for potential loss due to built-in potential (V_{bi}) and series resistance (V_{series}), and L is the active layer thickness.

Fabrication and characterization of inverted-type ethanol-processed PSCs: The inverted device with an ITO/ZnO/active layer/MoO$_3$/Ag architecture was used to evaluate the photovoltaic properties of ethanol-processed solar cells. ITO-coated glass substrates were subjected to ultra-sonication and cleaned with various solvents, i.e., acetone, deionized water,

and finally isopropyl alcohol. After the cleaning process, the substrates were kept in an 80 °C oven for 20 min. The ITO substrates were treated with UV-ozone (10 min) before spin-casting a ZnO layer. The ZnO solution was prepared by dissolving zinc acetate dihydrate $(Zn(O_2CCH_3)_2 \cdot (H_2O)_2$, 99.9%, 1 g) and ethanolamine $(HOCH_2CH_2NH_2$, 99.5%, 0.28 g) in anhydrous 2-methoxy ethanol $(CH_3OCH_2CH_2OH$, >99.8%, 10 mL) under vigorous stirring for > 24 h to allow the hydrolysis reaction and aging to occur. The ZnO solution was spin-coated on top of the ITO substrates at 4000 rpm to produce a 40 nm thick ZnO layer. After the films were baked at 200 °C for 10 min in ambient condition, the devices were moved to a N_2-filled glove box. Electron donor PPDT2FBT-A was blended with Bis-C_{60}-A electron acceptor in ethanol, where the D:A blend ratios were varied from 1:1 to 1:2 (w/w), and the concentration of the polymer donor in the blend solution was 5 mg mL^{-1}. The solutions were stirred for 1 h on a hot plate at 80 °C before spin-casting onto ITO/ZnO substrates at 1000 rpm for 40 s. The resulting thickness of the ethanol-processed blend film was measured to be 50−60 nm. The devices were baked for 20 min at 110 °C under vacuum for removal of residual ethanol in the active layer. The substrates were placed in an evaporation chamber under high vacuum (< 10^{-6} Torr) for ~1 h before deposition of MoO$_3$ (10 nm) and Ag (120 nm). The active area of the fabricated device was 0.09 cm^2, as measured by optical microscopy. The current density-voltage (*J-V*) characteristics of the devices were measured under AM 1.5G solar irradiation (100 mWcm^{-2}, Peccell: PEC-L01) at ambient condition. This solar simulator system satisfied the Class AAB, ASTM Standards. The intensity of the solar simulator was calibrated using a standard silicon reference cell with a KG-5 visible color filter. The *J-V* characteristics were measured using a Keithley 2400 SMU. The EQE data were obtained using a spectral measurement system (K3100 IQX, Mc Science Inc.) with monochromatic light from a xenon arc lamp at 300 W filtered by a monochromator

(Newport) and an optical chopper (MC 2000 Thor labs). The EQE data were acquired in the dark. The calculated J_{SC} value was acquired by integrating the product of the EQE and the AM 1.5G solar spectrum, and showed good agreement with the measured J_{SC}, within 2% error.
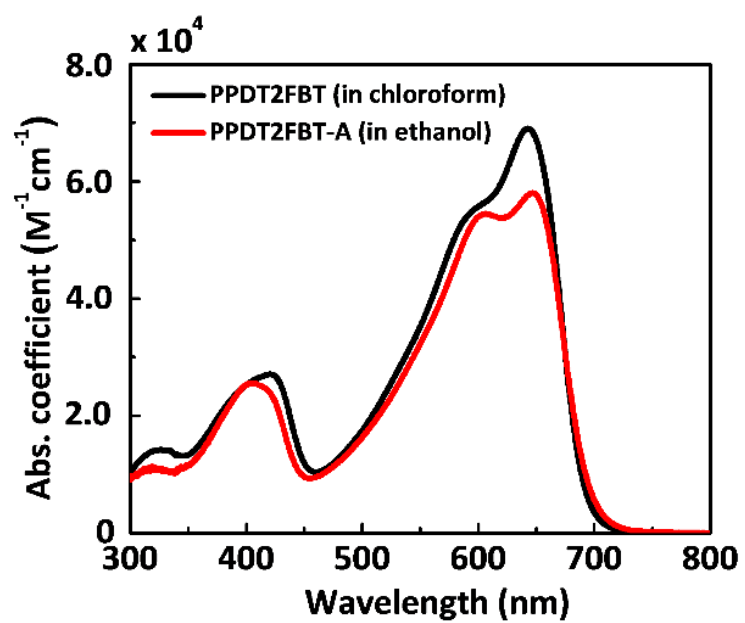
Supplementary Figure S1-7

Figure S1. Molar absorption coefficients of PPDT2FBT-A in ethanol and PPDT2FBT in chloroform.
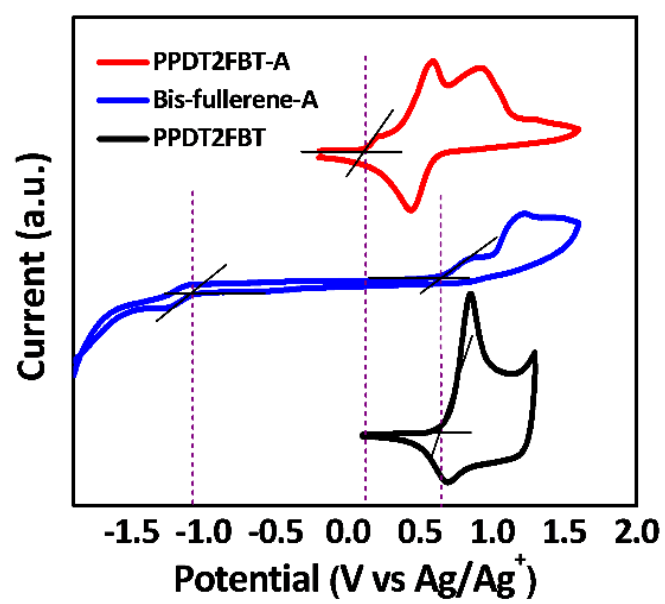
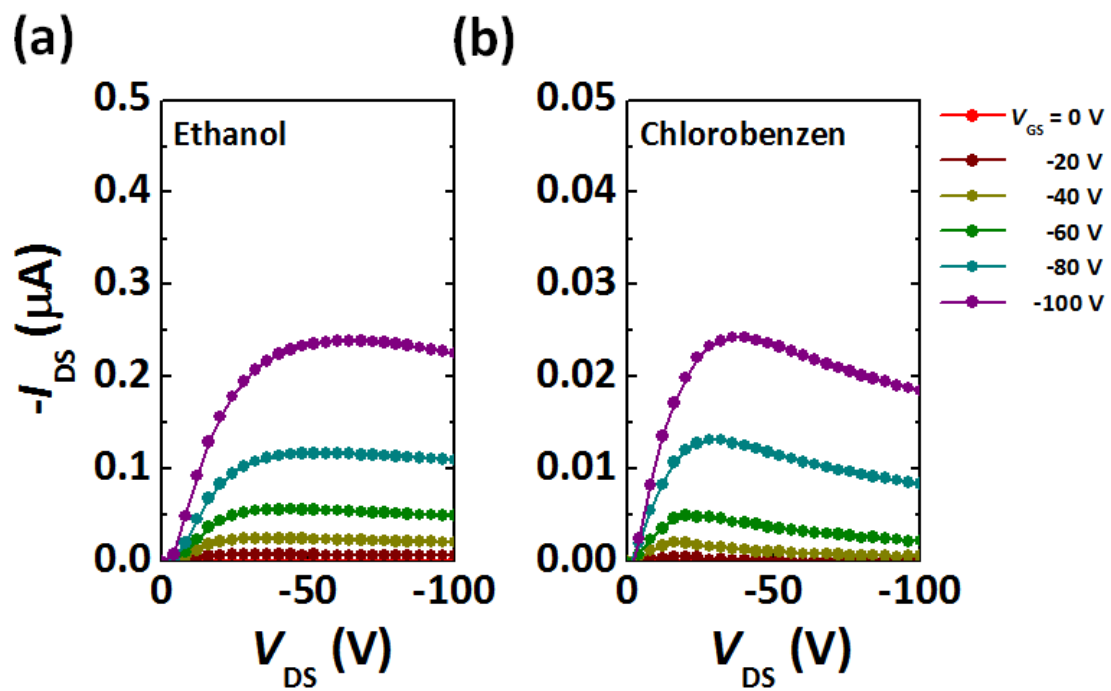**Figure S2**. Cyclic voltammograms of PPDT2FBT, PPDT2FBT-A and Bis-C$_{60}$-A.

Figure S3. Output curves of PPDT2FBT-A OFET devices fabricated using (a) ethanol or (b) CB as the processing solvent, respectively.
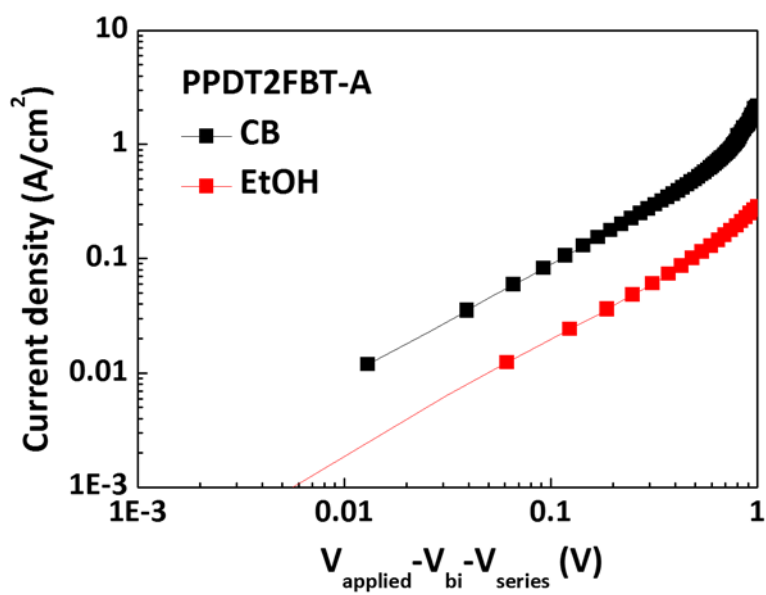
Figure S4. *J-V* characteristics of hole-only devices based on PPDT2FBT-A pristine films processed with CB (black line), EtOH (red line). Both devices were thermally annealed at 150 °C for 30 min.
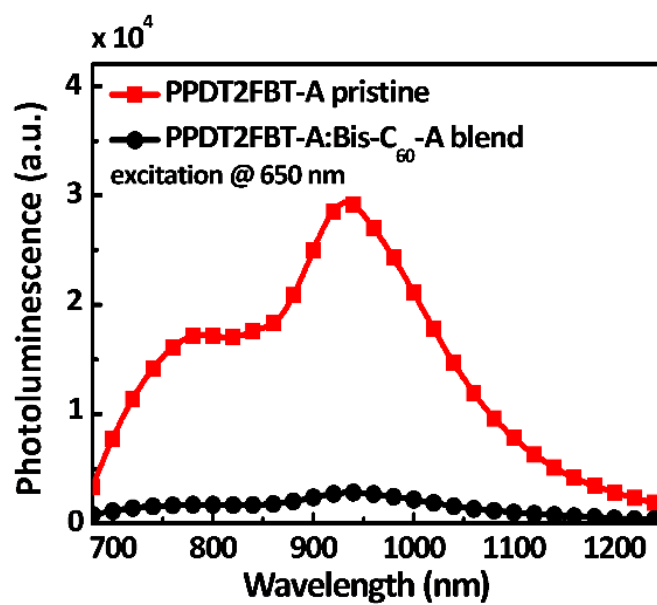
Figure S5. Photoluminescence of PPDT2FBT-A pristine polymer and PPDT2FBT-A:Bis-C_{60}-A blend films.
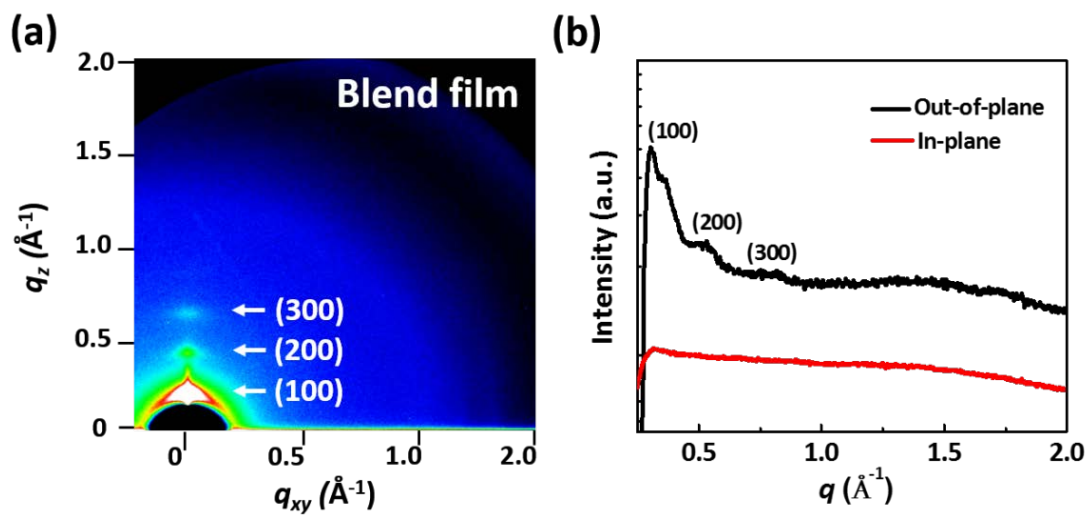
Figure S6. (a) 2D-GIXS pattern and (b) line profiles of PPDT2FBT-A:Bis-C$_{60}$-A blend film.
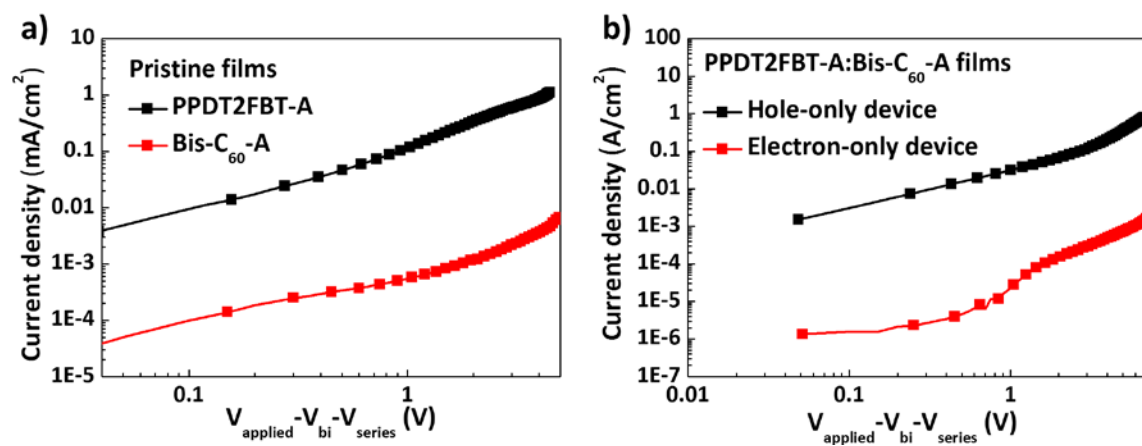
Figure S7. *J-V* characteristics of hole- and electron-only devices based on (a) PPDT2FBT-A and Bis-C_{60}-A pristine films, and (b) PPDT2FBT-A:Bis-C_{60}-A blend film.

Supplementary Table S1-4

Table S1. List of *median lethal dose (LD$_{50}$)* for various solvents.[4]

Solvent	Animal, route	Median lethal dose (LD$_{50}$)[a]
Ethanol	**rat, oral**	**10,470 mg/kg**
Acetone	rat, oral	5,800 mg/kg
Ethyl acetate	rat, oral	5,620 mg/kg
Toluene	rat, oral	5,580 mg/kg
Isopropyl alcohol	rat, oral	5,045 mg/kg
2-Methyltetrahydrofuran	rat, oral	4,500 mg/kg
1-Methyl-2-pyrrolidone	rat, oral	3,914 mg/kg
Anisole	rat, oral	3,700 mg/kg
Methanol	rat, oral	2,769 mg/kg
o-Xylene	mouse, intraperitoneal	1,364 mg/kg
1-Chloronaphthalene	rat, oral	1,540 mg/kg
Chlorobenzene	rat, oral	1,110 mg/kg
Chloroform	rat, oral	908 mg/kg
1,2-Dichlorobenzene	rat, oral	500 mg/kg

[a] Median lethal dose (LD$_{50}$): the amount of the substance required (per body weight) to kill 50% of the test population.

Table S2. Chemical list in the Toxic Release Inventory.[5]

Solvent	De minimus % Limit
Ethanol	-
Toluene	1.0
Isopropyl alcohol	1.0
1-Methyl-2-pyrrolidinone	1.0
Benzene	0.1
Methanol	1.0
o-Xylene	1.0
Chlorobenzene	1.0
Chloroform	0.1
1,2-Dichlorobenzene	1.0

Table S3. Summary of photovoltaic properties of the ethanol-processed devices with different PPDT2FBT-A:Bis-C_{60}-A blend ratios.

D:A weight ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE$_{avg}$ (%)
1:1	0.79±0.019	1.68±0.12	0.32±0.034	0.43±0.03
1:1.5	0.79±0.015	2.21±0.11	0.38±0.019	0.67±0.02
1:2	0.80±0.015	1.61±0.10	0.40±0.019	0.51±0.03

The average PCEs (± standard deviation) were derived from 10 different devices for each different system.

Table S4. Hole and electron mobilities of pristine and blend films measured by SCLC method

	$\mu_{\text{h, SCLC}}$ (max) ($\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$)	$\mu_{\text{h, SCLC}}$ (avg) ($\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$)	$\mu_{\text{e, SCLC}}$ (max) ($\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$)	$\mu_{\text{e, SCLC}}$ (avg) ($\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$)
PPDT2FBT-A	7.5×10^{-5}	5.0×10^{-5} ($\pm 2.6 \times 10^{-5}$)[a]	-	-
Bis-C$_{60}$-A	-	-	8.8×10^{-7}	5.3×10^{-7} ($\pm 2.7 \times 10^{-7}$)[a]
PPDT2FBT-A:Bis-C$_{60}$-A	2.6×10^{-5}	2.1×10^{-5} ($\pm 4.6 \times 10^{-6}$)[a]	2.3×10^{-8}	1.7×10^{-8} ($\pm 7.8 \times 10^{-9}$)[a]

The maximum and average mobilities obtained from at least 5 SCLC devices. [a] Standard deviation.

III. References

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