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Supporting Information

A 9,9'-Spirobi[9H-fluorene]-Cored Perylenediimide Derivative and Its Application in

Organic Solar Cells as Non-Fullerene Acceptor

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1. Experimental

1.1 Materials and measurements

Materials: All of the reagents and chemicals were purchased from commercial sources and used without further purification unless stated otherwise. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-n-octylfluorene (**Bpin-F-Bpin**) was purchased from SunaTech Inc. 2,2',7,7'-Tetrabromo-9,9'-spirobifluorene (**SBF-Br**₄) was purchased from Puyang Huicheng Electronic Material Co., Ltd. 2enthylhexylamine was purchased from Alfa Aesar, and 3,4,9,10-perylenetetracarboxylic dianhydride was purchased from Energy Chemical. 5-Bromo-2,9-bis(2-ethylhexyl)-anthra[2,1,9-*def*:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone (**Br-PDI**) was synthesized according to literatures.¹ [1,1'bis(diphenylphosphino)ferrocene] dichloropalladium(II) (**Pd(dppf)Cl**₂), anhydrous dichlorobenzene and chlorobenzene were purchased from Sigma-Aldrich, and used as received. [1,1'-bis(diphenyl phosphino)ferrocene]dichloropalladium(II) (**Pd(Pph**₃)₄) was purchased from J&K China Chemical Ltd. Anhydrous trichloromethane and dichloromethane were purchased from Sinopharm Chemical Reagent Co. Ltd, and were dried by distillation over calcium hydride. ZnO nanoparticles were synthesized according to literature procedures,² and were dispersed in acetone with a concentration of 10 mg·mL⁻¹ before used.

General Methods The ¹H NMR spectra were recorded in *d*-chloroform on a Varian MR 400 spectrometer (400 MHz), and the ¹³C NMR spectra were recorded on a Brucker Avance III 400 MHz NMR spectrometer. Chemical shifts are reported in δ (ppm), referenced to solvent residual peak (7.26 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR) as internal standard. The ¹³C NMR spectra of SBF-PDI₄ were recorded in *d*-1,1,2,2-tetrachloroethane at 100 °C on a Bruker DRX 400 NMR spectrometer. Matrix assisted laser desorption/ ionization time-of-flight mass spectrometry (MALDI-TOF) were

performed on a Brucker Autoflex Speed using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2propenylidene] malononitrile (DCTB) as the matrix. High resolution mass spectrometry (HRMS) was performed on a Thermo Fisher Scientific LTQ FT Ultra (operation mode: MALDI; matrix: 2,5dihydroxybenzoic acid). UV-vis spectra of these new materials in chloroform (CHCl₃) solution and thin film were recorded on a Perkin Elmer Lambda 750 UV-vis Spectrophotometer. For UV-vis absorption spectrum measurement in solution, three concentrated solutions (around 10⁻⁴ mol·L-1) were prepared independently, each of which were further diluted to get three diluted solutions (with concentration around 10⁻⁷-10⁻⁶ mol·L⁻¹) for UV-vis absorption measurement. The absorption spectra of the dilute solutions were recorded, and the data points of the absorbance at a certain wavelength vs. concentration were then plotted. A good linear relationship was found for all these compounds, suggesting no obvious intermolecular interaction was found in such a concentration range. The molecular molar extinction coefficient (ɛ) was obtained from the slope of the best-fit line over the above mentioned data points according to the Beer–Lambert's Law equation, A = ε ·L·c. Thin film samples for UV-vis spectra measurement were prepared by spin-casting a chloroform solution (around 1.0×10^{-3} mol·L⁻¹) on quartz glasses. Cyclic voltammetry (CV) experiments were performed with a RST-3000 Electrochemistry Workstation (Suzhou Risetech Instrument co., Itd). All CV measurements were carried out at room temperature with a conventional three-electrode configuration under nitrogen atmosphere. The electrochemical cyclic voltammetry was performed in a 0.1 mol·L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆)/dichloromethane (DCM) solution with a scan speed of 0.1 V·s⁻¹. A Pt disk (ϕ = 1 mm) embedded in Teflon was used as the working electrode. The surface was polished before use. A Pt sheet (~ 1 cm²) and Ag/AgCl were used as the counter and reference electrodes, respectively. A ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as an external standard. The concentration of PDI solution was 1.0×10^{-3} mol·L⁻¹ in DCM for CV measurement. AFM measurements were performed by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. Thin film samples for AFM measurement were deposited on ITO/ZnO substrates following the same procedures as used for OPV devices fabrication (*vide infra*). Transmission electron microscopy (TEM) tests were performed on a Tecnai G2 F20 STwin 200 kV fieldemission electron microscope (FEI). Specimens for the TEM experiments were obtained by transferring the floated blend films from the water onto the 200 mesh copper grid.

1.2 Fabrication and Characterization of OPV Cells

ITO-coated glass substrates were cleaned with detergent, de-ionized water, acetone, and isopropyl alcohol in turn by ultrasonic-wave cleaner, and then dried with a flow of nitrogen. After that, the substrates were treated in UV-ozone for 30 min to eliminate any remaining organic components. For inverted devices, a thin layer of ZnO (ca. 20 nm) was deposited onto pre-cleaned ITO-coated glass by spin-coating a solution of ZnO nanoparticles in acetone (filtered with a PTFE syringe filter, 0.45 µm) at 2300 rpm. The substrates were baked at 120 °C for 10 min in the nitrogen-filled glove box. Then, the active layer (the thickness about 100 nm) was deposited on ZnO surface by spin-coating a solution of active materials a speed of 1000 rpm (sustained 60 s). The active layers were natural drying and without any other post-processing. For preparation of the active layers, PTB7-Th and **SBF-PDI**₄ (**PDI-F-PDI**) were dissolved in anhydrous chloroform with different weight ratios at a total concentration of 8 mg·mL⁻¹ and stirred at room temperature for over 2h. In some cases, a certain volume of additive, such as (0.25%, 1%, 1.5%, 2%; v/v) 1-chloronaphthalene (CN), (0.5%, 1%, 2%; v/v) 1,8-diiodooctane (DIO) were dissolved in the solution prior to spin-coating/stirring. MoO₃ layer (ca. 20 nm) and Al (ca. 100 nm) were thermally deposited under a pressure of 1.0×10⁻⁴ Pa through a shadow mask on top of

active layer. The active area of the pixels, as defined by the overlap of anode and cathode is 0.09 cm².

Current density *vs* voltage curves (*J*–*V*) were measured under simulated solar light (100 mW·cm⁻ ²) from a tungsten-halogen lamp filtered by a UV Filter (Edmund Optics) and a Hoya LB120 daylight using a Keithley 2400 source meter.³ External quantum efficiency (EQE) were measured under simulated one sun operation conditions using bias light from a 532 nm solid state laser (Changchun New Industries, MGL-III-532). Light from a 150 W tungsten halogen lamp (Osram64610) was used as probe light and modulated with a mechanical chopper before passing the monochromator (Zolix, Omni- λ 300) to select the wavelength. The response was recorded as the voltage by an *I-V* converter (QE-IV Convertor, Suzhou D&R Instruments), using a lock-in amplifier (Stanford Research Systems SR 830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container.

1.3 Fabrication of electron-only devices

The electron-only devices were fabricated with a diode structure of glass/ITO/ZnO/PTB7-Th:**SBF-PDI**₄/LiF/Al. ITO-coated glass substrates were cleaned with the same method for fabrication of photovoltaic cells. ZnO layer was spin-coated (filtered with a PTFE syringe filter, 0.45 µm) onto precleaned ITO-coated glass substrates at 2300 rpm (ca. 20 nm). The substrates were baked at 120 °C for 10 minutes in the nitrogen-filled glove box. Then, the active layer was spin-coated under the same condition as for preparation of the optimal solar cell with different speeds on the ZnO surface. Finally, LiF (1 nm) and Al (100 nm) electrode were evaporated through mask on top of the active layer. Devices were tested by a Keithley 2400 source meter taking the dark current-voltage curve in the range of 0-8 V. The charge carrier mobilities were calculated using the space-charge limited current (SCLC) model,⁴ where the SCLC is described by:

$$J = 9\varepsilon_0\varepsilon_r\mu_e V^2/8d^3$$

where J is the current density, d is the film thickness of active layer, μ_e is the electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85 × 10^{-12} F·m⁻¹), V is the internal voltage in the device and $V = V_{appl} - V_r - V_{bi}$, where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes. The resistance of the device was measured using a blank configuration ITO/ZnO/LiF/AI.

1.4 Synthesis

1.4.1 Synthesis of 5-bromo-2,9-bis(2-ethylhexyl)-anthra[2,1,9-def:6,5,10-d',e',f']diisoquinoline-1,3,8,10(2H,9H)-tetrone (**Br-PDI**).

A mixture of 2,9-bis(2-ethylhexyl)-anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10 (2H, 9H)-tetrone (**EH-PDI**) (1.5 g, 2.4 mmol), potassium carbonate (4.0 g), and chlorobenzene (100 mL) were mixed in a 250 mL flask equipped with a condenser. Bromine (23.5 g, 146.9 mmol) was added dropwise. The reaction mixture was stirred at 60 °C for 2 days. The mixture was poured into 50 mL saturated Na₂SO₃ aqueous solution. It was then extracted with chloroform and the organic phase was washed with water and dried over anhydrous Na₂SO₄. The product as a red solid was purified by column chromatography on silica gel using dichloromethane as the eluent (767 mg, 1.11 mmol, 46%). **Br-PDI**: ¹H NMR (400 MHz, CDCl₃): δ = 9.66 (d, 1H, *J* = 8.0 Hz), 8.77 (s, 1H), 8.66 (m, 3H), 8.42 (dd, 2H, *J*₁ = 8.0 Hz, *J*₂ = 8.0 Hz), 4.10 (m, 4H), 1.93 (m, 2H), 1.45-1.20 (m, 16H), 0.95-0.85(m, 12H) ppm. 1.4.2 *Synthesis of 2,2',7,7'-tetra(2,2,3,3-tetramethyl-2,3-butanedionato)boron-9,9'-spirobifluorene* (**SBF-Bpin_4**)

2,2',7,7'-Tetrabromo-9,9'-spirobifluorene (SBF-Br₄) (1.5g, 2.37 mmol) and bis(2,2,3,3-

tetramethyl-2,3-butanedionato)diboron (3.5g, 13.78 mmol) were dissolved in dry 1,4-dioxane (30 mL) in a flask and then the reaction mixture was purged with N₂ for 30 min. [1,1'-bis(diphenyl phosphino)ferrocene]dichloropalladium(II) (**Pd(dppf)Cl**₂) (200 mg, 0.27 mmol) was added and the reaction mixture was stirred at 110 °C for 12 h under the N₂ atmosphere. After being cooled to room temperature, 1,4-dioxane was then evaporated using a rotary evaporator. The mixture was extracted with trichloromethane, washed with water, dried with anhydrous NaSO₄, filtrated and then evaporated. The crude product was purified by silica gel column chromatography with ethyl acetate and *n*-hexane (*v*:*v* = 1:3) as eluent, and then the product was purified again using dichloromethane/methanol recrystal. Compound 2,2',7,7'-tetra(2,2,3,3-tetramethyl-2,3-butanedionato)boron-9,9'-spirobifluorene (**SBF-Bpin₄**) (1.19 g, 1.45 mmol, 61% yield) was obtained as white solid.

SBF-Bpin⁴ ¹H NMR (400 MHz, CDCl₃): δ= 7.85 (m, 8H), 7.09 (t, *J* = 0.8 Hz, 4H), 1.25 (s, 48H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ=148.16, 144.68, 134.54, 130.44, 113.68, 83.65, 65.57, 24.78 ppm. MS (MALDI-TOF-MS): Calculated for C₄₉H₆₀B₄O₈, 820.5; Found, 820.6.

1.4.3 Synthesis of SBF-PDI₄

A mixture of 5-bromo-2,9-bis(2-ethylhexyl)-anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3, 8,10(2H,9H)-tetrone (**Br-PDI**) (800 mg, 1.15 mmol), 2,2',7,7'-tetra(2,2,3,3-tetramethyl-2,3-butanedionato)boron-9,9'-spirobifluorene (**SBF-Bpin**₄) (150 mg, 0.18 mmol), tetrakis(triphenyl-phosphine)palladium(0) (**Pd(Pph**₃)₄) (50 mg, 0.078 mmol), 30 mL toluene, 4 mL N,N-dimethyl-formamide (DMF) and 3 mL 1M K₃PO₄ solution was intensively stirred under nitrogen atmosphere at 120 °C for 2 days. The mixture was extracted with chloroform, washed with water, dried with anhydrous NaSO₄, filtrated and then evaporated. The crude product was purified by silica gel column

chromatography with dichloromethane and *n*-hexane (v:v = 10:1) as eluent and gel column chromatography with chloroform as eluent. Compound **SBF-PDI**₄ (330 mg, 0.12 mmol, 65% yield) was obtained as red solid.

SBF-PDI₄ ¹H NMR (400 MHz, CDCI₃): δ = 8.73 (s, 4H), 8.69 (d, *J* = 8.0 Hz, 4H), 8.46 (d, *J* = 7.6 Hz, 4H), 8.22 (s, 8H), 8.03 (d, *J* = 8.0 Hz, 4H), 7.35-7.28 (m, 8H), 7.24-7.18 (m, 4H), 6.95-6.89 (m, 4H), 4.30-4.12 (m, 8H), 3.72-3.60 (m, 4H), 3.42-3.28 (m, 4H), 2.05-2.15 (m, 4H), 1.57-0.83 (m, 104H), 0.83-0.78 (t, *J* = 7.2 Hz, 6H), 0.76-0.71 (t, *J* = 7.6 Hz, 6H) ppm. ¹³C NMR (100 MHz, C₂D₂Cl₄): δ =163.62, 162.71, 161.62, 142.90, 141.44, 140.98, 134.83, 133.88, 131.81, 131.79, 131.77, 130.53, 130.45, 128.85, 128.51, 127.75, 127.15, 126.25, 123.17, 122.41, 122.08, 119.02, 44.38, 43.45, 37.70, 37.50, 32.57, 31.77, 30.65, 29.57, 29.22, 28.63, 28.35, 23.06, 22.94, 22.83, 22.59, 14.16, 14.01, 10.62, 10.44, 10.34 ppm. MS (MALDI-TOF-MS): Calculated for C₁₈₅H₁₇₆N₈O₁₆, 2765.3; Found, 2766.2; Calculated for [M+Na]⁺ 2788.3; Found, 2789.2. HRMS: Calculated for C₁₀₉H₁₂₂N₄O₈, 2765.3204; Found, m/z = 2765.3168.

1.4.4 Synthesis of PDI-F-PDI

A mixture of 5-bromo-2,9-bis(2-ethylhexyl)-anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8, 10(2H,9H)-tetrone (**Br-PDI**) (119 mg, 0.17 mmol), 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-9,9-di-n-octylfluorene (**Bpin-F-Bpin**) (50 mg, 0.078 mmol), [1,1-bis(diphenyl phosphino)ferrocene] dichloropalladium(II) (**Pd(dppf)Cl**₂) (10 mg, 0.014 mmol), 5 mL 1,2-dimethoxyethane (DME) and 0.5 mL 1M K₂CO₃ solution was intensively stirred under nitrogen atmosphere at 85 °C for 5 h. The mixture was extracted with trichloromethane, washed with water, dried with anhydrous NaSO₄, filtrated and then evaporated. The crude product was purified by silica gel column chromatography with dichloromethane and *n*-hexane (*v*:*v* = 10:1) as eluent. Compound PDI-F-PDI (95 mg, 0.059 mmol, 75% yield) was obtained as dark red solid.

PDI-F-PDI (75% yield) ¹H NMR (400 MHz, CDCl₃):δ=8.78-8.61 (m, 10H), 8.22 (d, *J* = 7.6Hz, 1H), 8.10 (d, *J* = 8.0Hz, 1H), 8.06 (d, *J* = 8.4Hz, 1H), 8.03-7.96 (t, 3H), 7.61 (d, *J* =7.2 Hz, 1H), 7.59-7.52 (m, 2H), 7.49 (s, 1H), 4.28-4.05 (m, 8H), 2.07-1.86 (m, 8H), 1.52-1.27 (m, 32H), 1.18-0.99 (m, 24H), 0.98-0.86 (m, 24H), 0.82-0.67 (m, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ=163.83, 163.21, 153.28, 142.16, 141.94, 140.83, 136.13, 134.83, 130.99, 130.14, 128.07, 123.53, 123.07, 122.92, 122.67, 122.39, 122.17, 56.02, 44.43, 44.24, 38.04, 37.92, 30.84, 29.70, 29.28, 29.21, 28.77, 28.70, 24.15, 23.09, 22.60, 14.12, 14.04, 10.67, 10.58 ppm. MS (MALDI-TOF-MS): Calculated for C₁₀₉H₁₂₂N₄O₈, 1614.9; Found, 1615.2. HRMS: Calculated for C₁₀₉H₁₂₂N₄O₈, 1614.9257; Found, m/z = 1614.9266.

2. Supporting Figures and Scheme



Scheme S1 Synthetic route to PDI-F-PDI



Chart S1 Chemical structures of PTB7-Th and PDI-F-PDI



Fig. S1 DFT optimized geometries of SBF-PDI₄ (left) and PDI-F-PDI (right)



Fig. S2 DFT calculated LUMO and HOMO of SBF-PDI₄



Fig. S3 DFT calculated LUMO and HOMO of PDI-F-PDI

Supplementary discussion:

The geometries of SBF-PDI₄ and PDI-F-PDI were optimized using the Gaussian09 program with B3LYP/6-31G(d,p) approach. To simplify the models, the side chains were substituted with methyl. After energy minimization, the symmetry of SBF-PDI₄ and PDI-F-PDI are D_2 and C_2 respectively. As shown in Fig. S1, in PDI-F-PDI, the dihedral between PDI plane and the fluorene plane is 122.5 degree, while In SBF-PDI₄, due to the steric repulsion between PDI rings, the PDI rings align almost vertical (83.7 degree) to the adjacent fluorene plane.

The frontier molecular orbital (FMO) diagrams of SBF-PDI₄ and PDI-F-PDI are shown in Fig. S2 and Fig. S3. According to the calculated results, the FMOs of SBF-PDI₄ and PDI-F-PDI consist mainly of the molecular orbitals from the PDI rings. Since there are four PDI rings in SBF-PDI₄ and only two PDI rings in PDI-F-PDI, the HOMOs and LUMOs of SBF-PDI₄ are quasi quadra-degenerated, while those of PDI-F-PDI are quasi double-degenerated. The HOMO-LUMO gap of SBF-PDI₄ is 2.47eV, while that of PDI-F-PDI is 2.33eV. The lower energy gap of PDI-F-PDI is due

to the molecular orbital overlap between PDIs and the central fluorene, which results in an relatively higher HOMO in PDI-F-PDI.



Fig. S4 Normalized UV–vis absorption spectra of **SBF-PDI**₄ (film), PTB7-Th (film), PTB7-Th:**SBF-PDI**₄ blend (film) and the EQE curve of device ITO/ZnO/PTB7-Th:**SBF-PDI**₄ (1:1,*w*/*w*)/MoO₃/Al with 1% CN as additive.



Fig. S5 (a) Normalized UV-vis absorption spectra of **PDI-F-PDI** in thin film and in CHCl₃ solution. (b) Cyclic voltammetry (CV) of **PDI-F-PDI** (in dichloromethane solution, at 1.0×10^{-3} mol·L⁻¹, with 0.1 mol·L⁻¹ Bu₄NPF₆ as the supporting electrolyte)



Fig. S6 (a) Double logarithmic *J-V* curves of PTB7-Th:**SBF-PDI**₄ based electron-only device with the active layer thickness at 65 nm. Insert: Double logarithmic *J-V* curves of ITO/ZnO/PTB7-Th:**SBF-PDI**₄/LiF/Al electron-only devices with different PTB7-Th:**SBF-PDI**₄ thicknesses. (b) Linear correlations of lg(*J*) and lg(d) with a slope close to 3 for PTB7-

Th:**SBF-PDI**₄ based electron-only device confirming the space limited charge current when the voltage is higher than 0.5 V.



Fig. S7 AFM height (a, b, c, d, e, f, g) and phase images (a', b', c', d', e', f', g') of the PTB7-Th:**SBF-PDI**₄ blend films with different fabrication processes; without additive (a, a'), with 0.25% CN (b, b'), with 1% CN (c, c'), with 1.5% CN (d, d'), with 0.5% DIO (e, e'), with 1% DIO (f, f') and with 2% DIO (g, g'), respectively.



Fig. S8 AFM height (a, b, c, d, e) and phase images (a', b', c', d', e') of the PTB7-Th:**PDI-F-PDI** blend films with different fabrication processes; without additive (a, a'), with 1% CN (b, b'), with 2% CN (c, c'), with 0.5% DIO (d, d') and with 1% DIO (e, e'), respectively.



Fig. S9 TEM images of PTB7-Th:PDI-F-PDI blend films (a) without CN, (b) with 1% CN.



Fig. S10 (a) Normalized UV-vis absorption spectra of **SBF-PDI**₄ at different concentrations; (b) UV-vis absorption spectra of **SBF-PDI**₄ at different concentrations; (c) The fitting line of the data points of the absorbance (@ 499 nm) at a certain wavelength vs. concentration. (d) The fitting line of the data points of the absorbance (@ 535 nm) at a certain wavelength vs. concentration.



Fig. S11 (a) UV–vis absorption spectra of **PDI-F-PDI** at different concentrations; (b) The fitting line of the data points of the absorbance (@ 532 nm) at a certain wavelength vs. concentration.

3. Supporting Tables

Table S1. Photovoltaic properties of PTB7-Th:SBF-PDI4 and PTB7-Th:PDI-F-PDI with different ratios (v/v) of CN or

Entry	Acceptor	D/A	CN	DIO V _{oc}		J _{sc}		Best PCE	Aver. PCE ^a	
			(vol%)	(vol%)	(V)	(mA∙cm⁻²)	FF	(%)	(± std. dev.)(%)	
1		1.5:1			0.84	5.53	0.46	2.14	2.01 (±0.108)	
2		1:1				8.82	0.48	3.66	3.45 (±0.112)	
3		1:1.5			0.86	0.86 6.84 0.5		3.00	2.84 (±0.093)	
4		1:1	0.25		0.84	11.13	0.45 4.21		4.14 (±0.085)	
5		1:1	0.5		0.84	11.69	0.49	4.81	4.67 (±0.175)	
6	SBE-PDI4	1:1	1		0.85	0.85 13.08 0.48		5.34	5.26 (±0.102)	
7		1:1	1.5	0.83		11.75	0.51	4.97	4.83 (±0.129)	
8		1:1		0.5	0.82	2 5.53 0.48		2.18	2.12 (±0.079)	
9		1:1		1	0.82	4.22	0.46	1.61	1.45 (±0.153)	
10		1:1		2	0.82	3.91	0.35	1.12	1.03 (±0.105)	
11		1:1			0.84	8.27	0.36	2.49	2.44 (±0.045)	
12		1:1 0.5 0.8		0.86	10.13	0.42	3.66	3.43 (±0.275)		
13	PDI-F-PDI	1:1		1	0.86	8.65	0.41	3.05	2.82 (±0.216)	
14		1:1	1		0.82	10.52	0.46	3.97	3.85 (±0.108)	
15		1:1	2		0.83	8.93	0.42	3.11	2.98 (±0.124)	

DIO as additive using an inverted device structure.

^a Average values from over 8 pieces of devices. Tested under illumination of AM 1.5G 100 mW·cm⁻².

Table S2. Optoelectronic Parameters of PDI-F-PDI

Mater.	λ ^{sol.} [nm]ª	ε ^{sol.} [mol ⁻¹ ·L·cm⁻ ^{1]b}	λ ^{sol.} onset ^l [nm]ª	E ^{opt} (sol) [eV] ^c	λ ^{film} [nm] ^d	λ ^{film.} onset [nm] ^d	E ^{opt} (film) [eV] ^e	E ⁰ _{red1} E ⁰ _{red2} [V] [V]	E ^{onset} [V]	E ^{onset} [V]	E _{HOMO} [eV] ^f	E _{LUMO} [eV] ^g	Eg ^{cv} [eV] ^h
PDI-F-PDI	532	62,500	604	2.05	475,530	0 626	1.98	-1.16 -1.35	-1.08	0.92	-6.02	-4.02	2.00

^a In CHCl₃ solution (1.0 × 10⁻⁶ mol·L⁻¹); ^b Extinction coefficient in solution was obtained by linear fitting absorbance vs. concentration; ^c Optical band gap estimated from the absorption edge in solution, E_g^{opt} (eV) = 1240/ $\lambda_{onset}^{sol.}$ [nm]; ^d Spin-coated from CHCl₃ solution onto the quartz; ^e Optical band gap in solid film, E_g^{opt} (eV) = 1240/ λ_{onset}^{film} [nm]; ^f Calculated from the cyclic voltammograms, $E_{LUMO} = -[E_{red}^{onset} + 5.1]$ (eV) where the vacuum energy level of F_c^+/F_c was set as -5.1 eV; ^g Calculated from the $E_{HOMO} = -[E_{ox}^{onset} + 5.1]$ (eV); ^h E_g^{opt} (eV) = $E_{LUMO} - E_{HOMO}$.



4. Supporting figures for ¹H NMR, ¹³C NMR and MALDI-TOF-MS spectra

Fig. S12 ¹H NMR for SBF-PDI₄



Fig. S13 ¹³C NMR for SBF-PDI₄



Fig. S14 MALDI-TOF-MS of SBF-PDI4



Fig. S15 ¹H NMR for PDI-F-PDI



Fig. S16 ¹³C NMR for PDI-F-PDI



Fig. S17 MALDI-TOF-MS of PDI-F-PDI



Fig. S18 ¹H NMR for SBF-Bpin₄



Fig. S19¹³C NMR for SBF-Bpin₄



Fig. S20 MALDI-TOF-MS of SBF-Bpin4

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