Supporting Information

Nonfullerene Acceptor for Wide Band Gap Polymer Based Organic

Solar Cells

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S1.1 Experimental Part

Compound 6-bromo-2-octyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**1**)¹, 9-(2ethylhexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**3b**)², and 4,7-bis(5-bromothiophen-2-yl)-5-fluoro-6-((2-hexyldecyl)oxy)benzo[c][1,2,5]thiadiazole (**4b**)³ were synthesized by the literature reported before.



2-octyl-6-((trimethylsilyl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (2). A mixture of compound **1** (3.88 g, 10.0 mmol) and 50 mL triethylamine was degassed before and after (PPh₃)₂PdCl₂ (395 mg, 5.96 μ mol) and Cul (113 mg, 5.96 μ mol) was added. TMSA (1.47 g, 15.0 mmol) was injected to the reaction bottle by a syringe. After stirred at room temperature for 12 h, the solvent was removed under reduced pressure; the residue was partitioned between water (200 mL) and ethyl acetate (100 mL). The organic layer was separated; the aqueous layer was extracted with ethyl acetate (50 mL×3); and the combined organic layers were washed with brine (50 mL×3), dried over anhydrous MgSO₄, and evaporated to dryness. The residue was further purified by chromatography on silica gel with petroleum ether/ethyl acetate (10:1, v/v) as an eluent. After the product was dried under high vacuum, a

mixture of K₂CO₃ (6.9 g, 50.0 mmol), H₂O (1 mL) and methanol (50 mL) was added, and the mixture was stirred under N₂ protection for 1 h. Then the solvent was removal under reduced pressure; the residue was washed by brine and ethyl acetate; and the combined organic layers were dried over anhydrous MgSO₄ and evaporated to dryness. The residue was further purified by chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1, v/v) to yield **2** as a light yellow powder (2.16, 65%). ¹H NMR (400 MHz, C₆D₆): δ (ppm) 8.35-8.37 (d, *J* = 7.2 Hz, 1H), 8.18-8.22 (t, *J* = 7.6 Hz, 2H), 7.34-7.36 (d, *J* = 7.6 Hz, 1H), 7.08-7.13 (t, *J* = 8.0 Hz, 1H), 4.16-4.19 (t, *J* = 7.6 Hz, 2H), 3.22 (s, 1H), 0.81-1.76 (m, 15H). ¹³C NMR (100 MHz, C₆D₆): δ (ppm) 163.07, 162.77, 131.62, 131.28, 131.04, 130.90, 129.48, 127.19, 125.24, 123.31, 123.15, 86.08, 80.36, 40.36, 37.22, 35.14, 31.61, 28.23, 26.93, 22.68, 13.97.



6,6'-(buta-1,3-diyne-1,4-diyl)bis(2-octyl-1H-benzo[de]isoquinoline-1,3(2H)-dione) (**NI-AA-NI**). Compound **2** (3.33 g, 10.0 mmol) was dissolved in 50 mL triethylamine. The mixture was degassed and protected under N₂ atmosphere before and after Cul (113 mg, 5.96 µmol) was added. After reacted at room temperature for 12 h, the solvent was evaporated under reduced pressure. The residue was partitioned between water (200 mL) and dichloromethane (DCM, 50 mL). The organic layer was then washed with brine (50 mL×3), dried over anhydrous MgSO₄, and evaporated to dryness. The residue was further purified by chromatography on silica gel with DCM as an eluent to afford compound **2** as a yellow solid (2.32 g, 70%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.58-8.59 (m, 2H), 8.56-8.57 (d, *J* = 6.4 Hz, 1H), 8.03-8.06 (d, *J* = 6.0 Hz, 1H), 7.87-7.91 (t, *J* = 5.6 Hz, 1H), 4.16-4.20 (t, *J* = 7.6 Hz, 2H), 0.87-1.74 (m, 15H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 163.64, 163.35, 132.56, 132.22, 131.81, 129.97, 128.05, 127.90, 125.12, 123.41, 123.21, 81.95, 81.50, 77.21, 40.68, 31.80, 29.32, 29.21, 28.10, 27.14, 22.63, 14.08. Anal. calcd for C₄₄H₄₄N₂O₄ (%): C, 79.49; H, 6.67; N, 4.21. Found (%): C, 79.32; H, 6.81; N, 4.03.



P1. A mixture of compound 3a (159 mg, 0.30 mmol), compound 4a (248 mg, 0.30 mmol), NaHCO₃ (1.25 g, 9.0 mmol), THF (20 mL), toluene (7 mL), and H₂O (2 mL) was degassed before and after Pd(PPh₃)₄ (6.9 mg, 6.0 µmol) was added. The mixture was heated to reflux and stirred for 3 d under nitrogen atmosphere. Then phenylboronic acid (10.0 mg) and bromobenzene (0.20 mL) were added successively at a time interval of 5 h to end-cap the bromo and boronic acid ester end groups, respectively. After cooled down to room temperature, the mixture was poured into acetone (100 mL), and the resulted precipitates were collected by filtration and washed with acetone (15 mL) for three times. The precipitates were dissolved in hot chlorobenzene and filtrated. After removing most solvent, the concentrated solution was precipitated into acetone (200 mL). The precipitates were collected by filtration; extracted on Soxhlet apparatus with methanol, hexane, and chloroform; and airdried overnight to afford **P1** as a dark red solid (240 mg, 84%). GPC (PS standards): $M_w = 50.3$ kg mol⁻¹, $M_n = 20.1$ kg mol⁻¹, and PDI = 2.50.

P2. A mixture of 3b (159 mg, 0.30 mmol), compound 4b (215 mg, 0.30 mmol), NaHCO₃ (1.25 g, 9 mmol), THF (20 mL), toluene (7 mL), and H₂O (2 mL) was degassed before and after Pd(PPh₃)₄ (6.9 mg, 6.0 μ mol) was added. The mixture was heated to reflux and stirred for 3 d under N₂ atmosphere. Phenylboronic acid (10 mg) and bromobenzene (0.2 mL) were added successively at a time interval of 12 h to end-cap the bromo and boronic acid end groups, respectively. After cooling down to room temperature, water (100 mL) and chloroform (100 mL) were added. The organic layer was separated, washed with water (50 mL × 3), and concentrated by evaporation of most of the solvent. The residue was poured into a large amount of acetone, and the resulting precipitates were collected by filtration and washed with

acetone. The crude product was dissolved in a large amount of hot chlorobenzene and filtrated. After the removal of most of the solvent, the resulted concentrated solution was precipitated into a large amount of acetone. The precipitates were collected by filtration and dried under vacuum to obtain **P2** as a dark-red solid (201 mg, 74%). GPC (PS standards): $M_{\rm w} = 119.1$ kg mol⁻¹, $M_{\rm n} = 48.1$ kg mol⁻¹, and PDI = 2.48.

S1.2 Measurements and characterization

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere and monitored by thin layer chromatography (TLC) on silica gel plates. ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 spectrometer. UV-visible absorption spectra were measured on a PerkinElmer UV-vis spectrometer model Lambda 750. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on TA2100 and Perkin-Elmer Diamond differential scanning calorimetry (DSC) instrument, respectively, under an atmosphere of nitrogen at a heating rate of 10 °C/min. Atomic force microscopy (AFM) measurements were carried out under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA using the tapping mode. The thickness of blend films was measured by a Dektak 6 M surface profilometer. XRD experiments were carried out by X' Pert PRO MPD instrument. The electrochemical behavior of polymers was studied using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a three-electrode electrochemical cell in a 0.1 M Bu_4NPF_6 CH₃CN solution under an atmosphere of nitrogen with a scanning rate of 0.1 V/S. A glassy carbon working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ (0.01 M in CH₃CN) reference electrode were used. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the internal reference standard. HOMO energy level was determined according to the equation E_{HOMO} = -e $[E_{ox} + 4.80 - E(Fc/Fc^{+})]$. HOMO level was calculated by the equation $E_{LUMO} = E_{HOMO} + E_{LUMO}$ Eg,opt.

S1.3 Polymer Solar Cells Fabrication and Characterization

PSCs were fabricated with the device configuration of ITO/PEDOT:PSS (30 nm)/P1-2:NI-AA-NI/LiF (0.7 nm)/Al (100 nm). The conductivity of ITO is 15 Ω . PEDOT:PSS (Baytron Al 4083 from H.C. Starck) was filtered with a 0.45 mm polyvinylidene difluoride (PVDF) film before use. A PEDOT:PSS thin layer was spin-coated on top of the cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130 °C for 20 min on a hotplate. The thickness of the PEDOT:PSS layer is about 30 nm. A mixture of donor polymer and NI-AA-NI in 1,2-dichlorobenzene (DCB) was stirred at 90 °C temperature overnight to ensure sufficient dissolution and then the blend solution was spin-coated onto PEDOT:PSS layer to form the active layer. A top electrode of 0.7 nm LiF and 100 nm of aluminum were thermally evaporated at a pressure of 10⁻⁴ Pa through a shadow mask. On one substrate five cells with an effective area of 0.04 cm² for each were fabricated. Current-voltage (I-V) and external quantum efficiency (EQE) measurements were conducted in air without encapsulation. I-V characteristics were recorded at room temperature using an Agilent B2902A Source Meter under the illumination of an AM1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mW cm⁻² and the white light intensity was calibrated with a standard single-crystal Si solar cell. Devices were stored in the glove box without encapsulation and periodically tested for 7 days to investigate the photovoltaic performance.

S1.4 Space-Charge Limited Current Measurement

Hole-only devices with a structure of ITO/PEDOT:PSS (30 nm)/ **P1-2:NI-AA-NI** /Au (100 nm) and electron-only devices with a configuration of FTO/ **P1-2:NI-AA-NI** /AI (100 nm) were fabricated. FTO substrates were prepared by etching the commercial FTO substrates with HCl and Zn powders. The blend solution of donor polymer and **NI-AA-NI** in 1,2-dichlorobenzene (DCB) was spin-coated onto PEDOT:PSS layer to form the active layer like PSC devices, and 100 nm of Au was thermally evaporated at a pressure of 10⁻⁴ Pa through a shadow mask. For electron-only devices, the blend solution of donor polymer and **NI-AA-NI** in 1,2-dichlorobenzene (DCB) was spin-coated on the clean FTO substrates to form active layer. Al electrodes (100 nm) were vacuum deposited on polymer thin films. Dark J–V curves of the hole-only devices and electron-only devices were measured by the space-charge limited current (SCLC) method. Dark *J–V* curves of devices were fitted by using the Mott–Gurney equation:

 $J = 9\varepsilon_o\varepsilon_r\mu V^2/8L^3$, where J is the space charge limited current, ε_o is the vacuum permittivity, ε_r is the permittivity of the active layer, μ is the hole mobility or the electron mobility, and L is the thickness of the active layer.



Fig. S1 TGA images of P1, P2, and NI-AA-NI.



Fig. S2 DSC images of NI-AA-NI.



Fig. S3 XRD images of NI-AA-NI.



Fig. S4 Cyclic voltammetry curves of **P1**, **P2**, (a) and **NI-AA-NI** (b) as thin films on glassy carbon working electrodes and cyclic voltammetry spectra of Fc/Fc^+ (c).



Fig. S5 PCE plotted versus storage time for OSCs based on polymer:**PC₇₁BM**, and polymer:**NI-AA-NI**.



Fig. S6 $J^{1/2}$ –V curves of hole only devices (a) and electron only devices (b).



Fig. S7 AFM images of blend films as spin-coated (a) **P1:NI-AA-NI** (b) **P2:NI-AA-NI** and with 0.5% 1-CN (a1) **P1:NI-AA-NI** (b1) **P2:NI-AA-NI**.



Fig. S8 ¹H NMR spectrum of NI-AA-NI (measured in CDCl₃).



Fig. S9 ¹³C NMR spectrum of NI-AA-NI (measured in CDCl₃).

Table S1. Detailed parameters of the optimized geometry of **NI-AA-NI** from DFT calculations (B3LYP/6-31G(d)).

Acceptor	NI1//A1	A1//A2	A2//NI2	NI1//NI2
NI-AA-NI	0.79	5.85	0.79	0.31

References

- 1. Z. Chen, X. Liang, H. Zhang, H. Xie, J. Liu, Y. Xu, W. Zhu, Y. Wang, X. Wang and S. Tan, *Journal of medicinal chemistry*, 2010, **53**, 2589-2600.
- 2. S.-Y. Liu, H.-Y. Li, M.-M. Shi, H. Jiang, X.-L. Hu, W.-Q. Li, L. Fu and H.-Z. Chen, *Macromolecules*, 2012, **45**, 9004-9009.
- 3. G. Li, B. Zhao, C. Kang, Z. Lu, C. Li, H. Dong, W. Hu, H. Wu and Z. Bo, ACS Applied Materials & Interfaces, 2015, **7**, 10710-10717.