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Supporting Information

Naphthalimide end capped imide-fused benzothiadiazole based small molecule acceptor for organic solar cells

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Experimental section

Measurement and characterization

^{1}H and ^{13}C NMR spectra were measured on Bruker-300 spectrometer. Chemical shifts were reported as d value (ppm) relative to an internal tetramethylsilane (TMS) standard. The thermal stability of small molecule was evaluated on TGA Q50 in nitrogen, with a heating rate of 20 ^{o}C/min. UV-vis absorption spectra were recorded on a UV 2450 Spectrophotometer and a PerkinElmer Lambda 750 UV/Vis/NIR Spectrometer. Photoluminescene (PL) spectra were measured using a HITACHI F-4600 FL spectrophotometer. Cyclic voltammograms measurements (CV) were recorded on a CHI 660A electrochemical workstation. The CV measurements was carried out in an anhydrous and nitrogen-saturated acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophospate (Bu_4NPF_6) as the supporting electrolyte, using a Ag/Ag+ (0.1 M $AgNO_3$ in acetonitrile) and a platinum wire as the reference and counter electrode, respectively, at a scan rate of 100 mV/s at room temperature. The platinum electrode coated with thin copolymer film was used as the working electrode. Atomic force microscopy (AFM) measurements were carried out using a DI MultiMode Nanoscope-Ⅲa (Veeco Instruments) system in taping mode.

Device fabrication and characterization

Patterned indium tin oxide (ITO)-glass substrates were used as the anode in the organic solar cells. The ITO coated glass substrates were cleaned by sequentially sonication with detergent, deionized water, acetone, and isopropyl alcohol, and then dried in oven at 100 ^{o}C, followed by an oxygen plasma for 10 min. Then the surface of the ITO substrate was modified by spin coating the conducting ZnO layer with a thickness of 40 nm, followed by baking on a hotplate at 200 ^{o}C for 60 minutes. Then the substrates were transferred into a nitrogen-filled glovebox. The P3HT:**BIBT-NI** blends were obtained by spin coating the *o*-dichlorobenzene (*o*-DCB) solution with or without 1v/v % 1,8-diiodoctane (DIO) at the blend concentration of 28 mg mL^{-1}. The film thicknesses of the active layer were around 90 nm. Thermal annealing of the blend films was carried out by placing them onto a hot plate with 110 ^{o}C for 10 minutes in a nitrogen atmosphere. Finally, about 10 nm molybdenum oxide (MoO_3) was thermally deposited on top of the P3HT:**BIBT-NI** layer through a shadow mask in a vacuum chamber with base pressure of 3×10^{-4} Pa. The effective area of the device was 0.16 cm^2 as determined by the shadow mask used during deposition of Al cathode.

The power conversion efficiencies of the resulting organic solar cells (OSCs) were measured under 1 sun, AM 1.5 G (air mass 1.5 global) spectrum from a solar simulator (Newport Solar Simulator 94021A) (100 mW cm^{-2}). The current density–voltage (*J–V*) characteristics were recorded with a Keithley 2400 source measure unit. The external quantum efficiencies of OSCs were measured with a commercial EQE measurement system (QTEST 1000 AD, Crowntech Inc.).

Space charge limited current (SCLC) measurement

Hole-only and electron-only devices were fabricated to measure the hole and electron mobilities using the space charge limited current (SCLC) method with a device configuration of ITO/PEDOT:PSS/active layer/MoO_3/Al and ITO/ZnO/active layer/Ca/Al, respectively. For hole-only device, the PEDOT:PSS layer was spin-cast onto the pre-cleaned ITO glass followed by thermal annealing at 150 ^{o}C for 15 min under ambient conditions. The substrates were then transferred into an N_2-filled glovebox. Subsequently, the BHJ composite films were prepared on ITO/PEDOT:PSS substrates using the same method as that for solar cell device fabrication. Finally, MoO_3 (~10 nm) and Al (~100 nm) were sequentially thermally deposited on the top of the active layer in a vacuum system. For electron-only device, the BHJ composite films were prepared on ITO/ZnO substrate using the same method as that for solar cell device fabrication. Then Ca (~4 nm) and Al (~100 nm) were sequentially thermally deposited on the top of the active layer in a vacuum system. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, described by the equation: $J_{SCLC} = (9/8)\varepsilon_0\varepsilon_r\mu_0(V^2/L^3)$, where J was the current, μ_0 is the zero-field mobility, ε_0 was the permittivity of free space, ε_r was the relative permittivity of the material, L was the thickness of the active layer, and V was the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The hole-mobility and electron-mobility can be calculated from the slope of the $J^{1/2}$–V curves.

Materials

All the chemicals and reagents were purchased from from commercial sources (Aldrich, Acros, and Alfa Aesar) and used without further purification unless stated otherwise. All the reactions were carried out under argon at 1 atm unless mentioned otherwise. Tetrahydrofuran (THF) was distilled from sodium before use. The donor material of P3HT was purchased from Nichem Fine Technology Co. Ltd. The weight average molecular weight (M_w) of P3HT was 68000. The compounds of N-(2-ethylhexyl)-4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-dicarboxylic imide (5) and 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(2-ethylhexyl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (3') were synthesized according to the methods reported previously.[1,2]

Synthesis of ***6***

Compound 5 (0.96 g, 2 mmol) was dissolved in chloroform (30 mL) and glacial acetic acid (10 mL), and then N-bromosuccinimide (NBS) (1.07 g, 3 mmol) was added in several portions. The mixture was stirred for 24 h at room temperature. The mixture was extracted with CH_2Cl_2, the combined organics were dried with anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The crude product was purified by silica column chromatography and recrystallization from ethanol afforded the title compound as a red solid (0.97 g, yield = 76%). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.78 (d, 2H), 7.22 (d, 2H), 3.63 (d, 2H), 1.87 (m, 1H), 1.24–1.38 (m, 8H), 0.86 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 165.94, 156.01, 134.03, 133.06, 129.86, 126.34, 125.92, 118.64, 42.98, 38.09, 30.64, 28.52, 23.99, 23.02, 14.06, 10.46.

Synthesis of ***BIBT-NI***

To a two-necked round-bottomed flask (150 mL) was added **6** (0.40 g, 0.63 mmol), **3’** (0.69 g, 1.58 mmol), tetrahydrofuran (80 mL) and 2 M aqueous K_2CO_3 solution (20 ml) under argon. The mixture was purged with argon for 20 min. Then catalyst $Pd(PPh_3)_4$ (25 mg) was quickly added under a stream of argon, and the mixture was purged with argon for another 15 min. Subsequently, the reaction mixture was heated to reflux for 18 h with stirring. Then the reaction mixture was cooled to ambient temperature and extracted with CH_2Cl_2 and H_2O. The organic layer was dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified using silica column chromatography with a mixture of petroleum ether and dichloromethane as eluent. Then the crude product recrystallized from hot methanol to get **BIBT-NI** as a deep red solid (0.45 g, yield = 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.80 (d, 2H), 8.65 (m, 4H), 8.15 (d, 2H), 8.00 (d, 2H), 7.81 (t, 2H), 7.53 (d, 2H), 4.16 (d, 4H), 3.71 (d, 2H), 1.97 (m, 3H), 1.25–1.43 (m, 24H), 0.89 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 166.13, 164.53, 164.28, 156.26, 145.07, 138.17, 134.41, 133.73, 132.25, 131.58, 130.70, 129.81, 128.95, 128.83, 128.58, 127.46, 126.65, 126.40, 123.11, 122.50, 44.29, 38.19, 37.98, 30.80, 30.69, 28.75, 28.54, 24.12, 24.06, 23.10, 23.07, 14.12, 14.09, 10.70, 10.53.

Additional figures

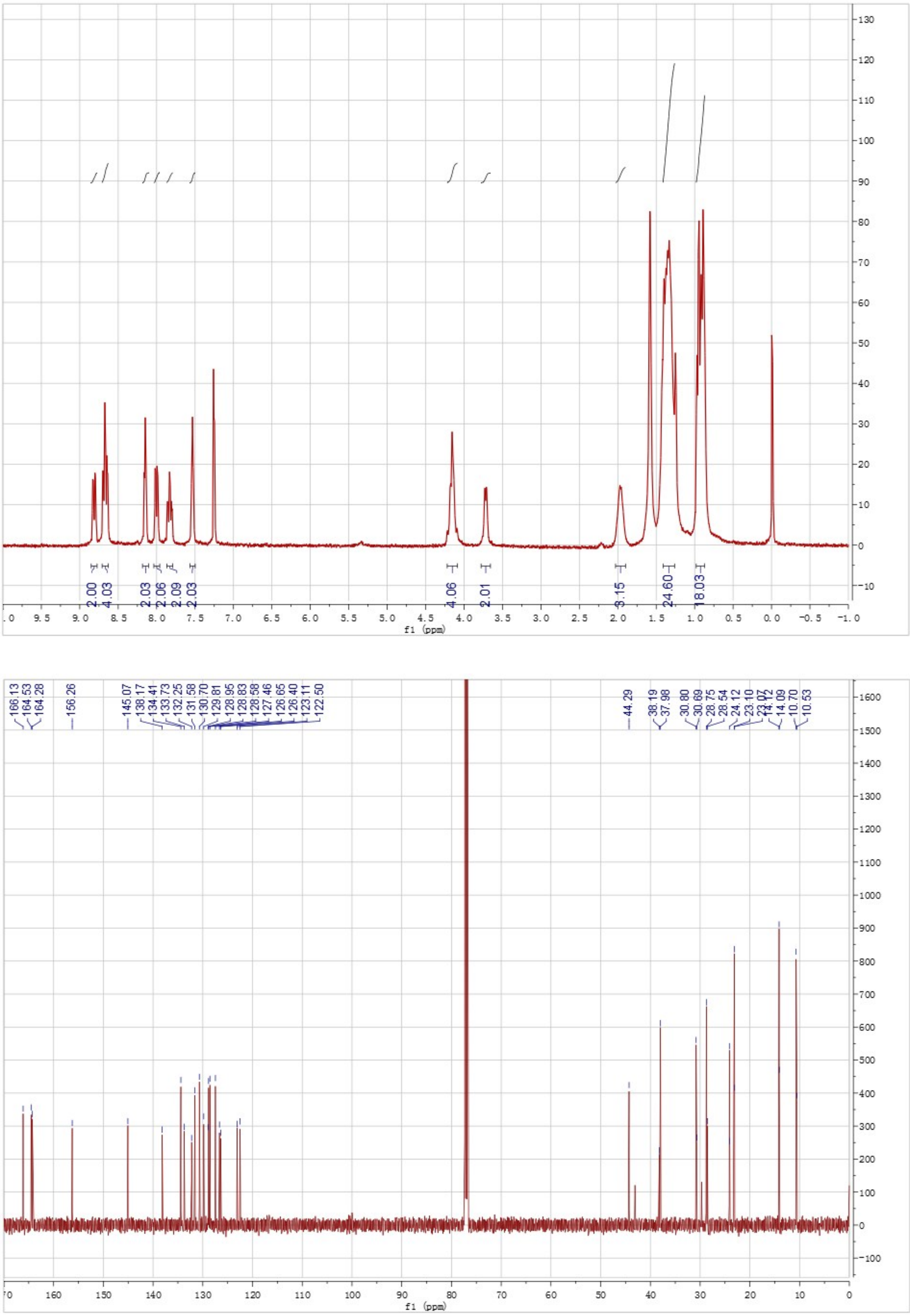

Fig. S1. ^{1}H and ^{13}C NMR spectra of **BIBT-NI**.

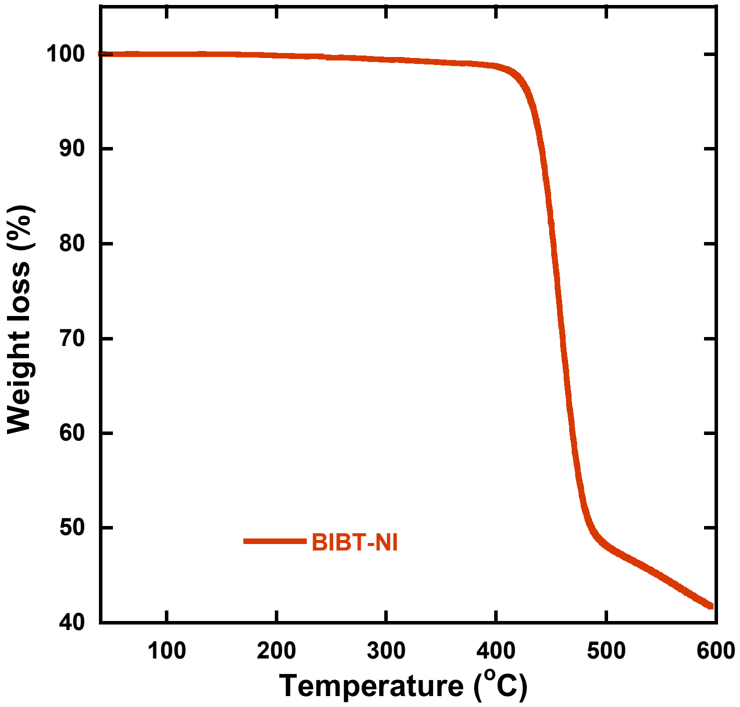

Fig. S2. TGA plot of **BIBT-NI** with a heating rate of 20 °C/min under inert atmosphere.

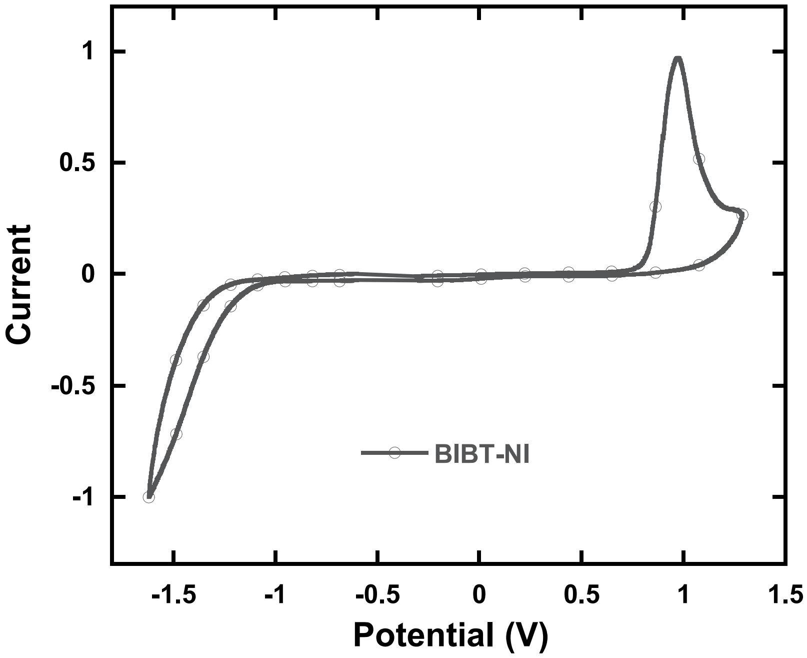

Fig. S3. Cyclic voltammograms (CV) of the **BIBT-NI** film on the Pt electrode in 0.1 M Bu_4NPF_6 acetonitrile solution at 100 mV/s.

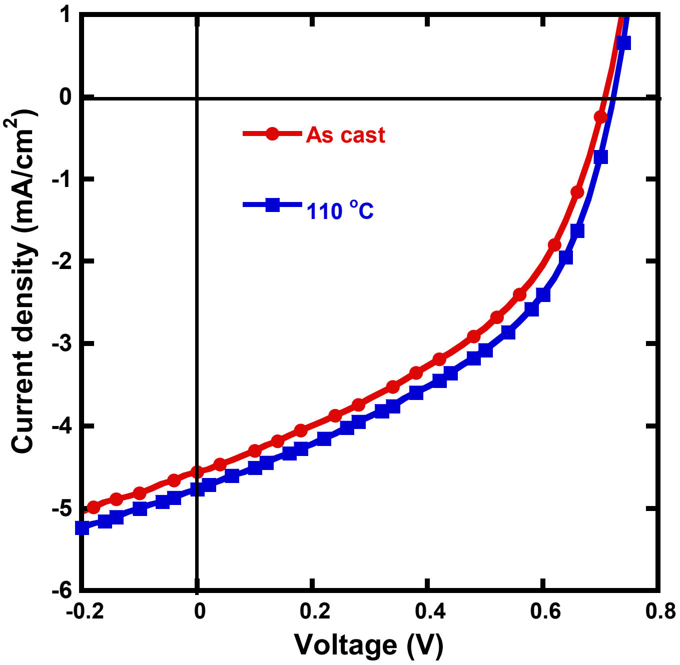

Fig. S4. *J-V* curves of the OSCs with the active layer processed from *o*-DCB solution containing 1 v/v% DIO in inverted device structure of ITO/ZnO/P3HT:**BIBT-NI** (w/w, 1:1.2)/MoO_3/Al

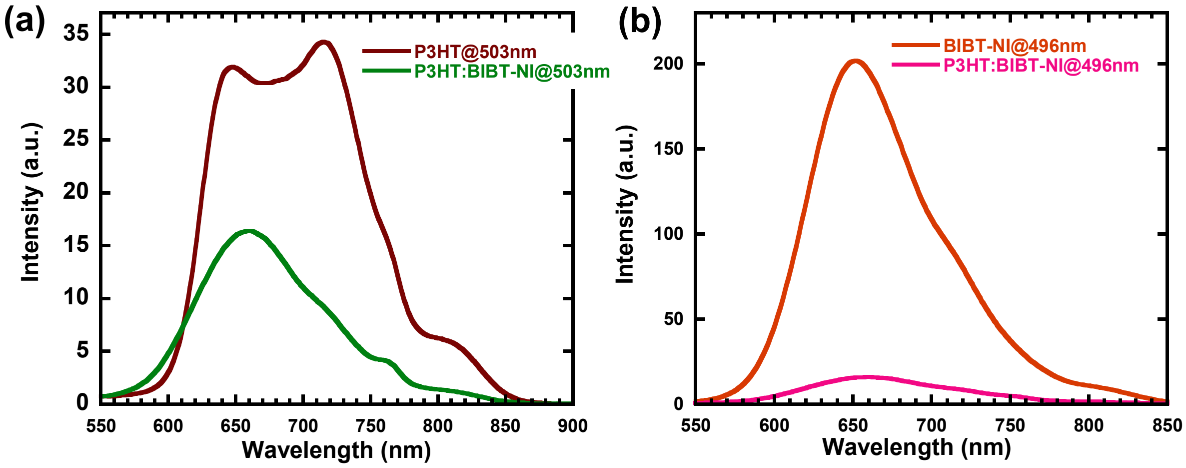

Fig. S5. Photoluminescence spectra of (a) P3HT and the blend film of P3HT:**BIBT-NI** (1:1.2, w/w) with thermal annealed at 110 °C (excited at 503 nm); (b) **BIBT-NI** and the blend film of P3HT:**BIBT-NI** (1:1.2, w/w) with thermal annealed at 110 °C (excited at 496 nm).

Additional Table

Table S1. Photovoltaic performances of devices with the structure of ITO/ZnO/P3HT:**BIBT-NI** (w/w, 1:1.2)/MoO_3/Al with the active layer processed from *o*-DCB solution containing 1 v/v% DIO

Active layer	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE$^{a)}$ [%]	PCE$_{max}$ [%]
As cast	0.71±0.01	4.42±0.18	43.0±0.9	1.36±0.06	1.42
110°C thermal annealed	0.73±0.01	4.72±0.06	44.3±1.0	1.52±0.03	1.54

$^{a)}$ The average PCE value was calculated from 10 devices.

References

1 L. Y. Lan, Z. M. Chen, L. Ying, F. Huang, Y. Cao, *Org. Electron.*, 2016, **30**, 176.

2 Q. J. Zhang, J. H. He, H. Li, N. J. Li, Q. F. Xu, D. Y. Chen, J. M. Lu, *J. Mater. Chem. C*, 2017, **5**, 7961.