Supporting Information

A Novel Naphthalene Diimide-based Conjugated Polymer as Electron Transport Material for Non-Fullerene Organic Solar Cells

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The synthesis and characterization details of PNDI-NN.

1) Materials

Thiophene and N,N-dimethyldipropyltriamine were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. n-Butyllithium, tributyltin chloride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 2-bromothiophene and tetratriphenylphosphine palladium were purchased from Shanghai Energy Chemical Co., Ltd. 1,3-Dibromo-5,5-dimethylhydantoin was purchased from McLin. Concentrated sulfuric acid of 96% specification was purchased from Sinopharm Chemical Reagent Co., Ltd. Acetic acid was purchased from Shanghai Mairuier Chemical Technology Co., Ltd. 3,3'-Difluoro-2,2'-bithiophene-5,5'-diylbis(trimethylstannane) was purchased from Derthon Optoelectronic Materials Co., Ltd.

2) Synthesis of intermediate products

Thiophene (6.65 g, 0.079 mol) was dissolved in tetrahydrofuran (50 mL) under argon atmosphere, and n-butyllithium (30 mL, 0.072 mol, 2.4 mol/L) was added into the system at -78 °C and the solution was stirred for 1 h. Tributyltin chloride was added to react for another hour, and the system was placed at room temperature for 8 h. Water was added to the mixture. After full oscillation, petroleum ether was added for three extractions. The organic phase was combined, dried and filtered. Under reduced pressure, the solvent was removed. After drying in vacuum, 32.38 g of light yellow liquid was obtained and used directly for the next reaction. $^1$H NMR (100 MHz, CDCl$_3$, ppm): $\delta$ = 7.67 (dd, 1H), 7.29 (dd, 1H), 7.23(t, 1H), 1.56-1.65(m, 6H), 1.30-1.43(m, 6H), 1.09-1.18(m, 6H), 0.88-0.98(m, 9H).

2,6-Dibromo-1,4,5,8-naphthalenetetracarboxylic dianhydride (2.707 g, 10.09 mmol) was stirred evenly in concentrated sulfuric acid (25 mL, 96%). 1,3-Dibromo-5,5-dimethylhydantoin (g, mmol) was added into the mixture in batches within one hour, and stirred at 50 °C for 24 hours. The mixture was poured into broken ice and diluted with water. The precipitate was filtered and washed several times with water. After drying in vacuum, 3.357 g of yellow solid was obtained with a yield of 78%. $^1$H NMR (100 MHz, DMSO-d$_6$, ppm): $\delta$ 8.76 (s, 2H).
1,4,5,8-Naphthalenetetracarboxylic dianhydride (1.000 g, 2.35 mmol) was mixed uniformly in acetic acid (30 mL), then N,N-dimethyldipropyltriamine (0.935g, 5.87 mmol) was added and stirred at 130 °C for 45 min. After the reaction was completed, the mixture was poured into cold water, neutralized with K₂CO₃, and extracted with CHCl₃. Under reduced pressure, the solvent was removed. The residue was separated by silica gel column chromatography with CH₂Cl₂:MeOH:NEt₃ (volume, 50:10:1) as eluent. Finally, light yellow solid NDI-NN (1.026 g, yield 79.5%) was obtained.

3) Synthesis of the Copolymer PNDI-NN.

3,3'-Difluoro-2,2'-bithiophene-5,5'-diyl)bis(trimethylstannane) (101 mg, 0.19 mmol), NDI-NN (105 mg, 0.19 mmol), and palladium tetratriphenylphosphine (10 mg, 0.009 mmol) were mixed in N,N-dimethylformamide (DMF)/Tol (3 mL/2 mL) under argon atmosphere. After refluxing for 48 h, a drop of tributyl(thiophen-2-yl)stannane was added and refluxed for another 12 h. Then two drops of 2-bromothiophene was added, and then reacted for 12 h. The mixture was dissolved in a small amount of methanol and precipitated in petroleum ether. After filtration, the filter cake was successively washed with petroleum ether, acetone, chloroform and methanol. The methanol solution was concentrated and poured into massive acetone to obtain blue-violet solid (50 mg, yield 60.2%). 1H NMR (CDCl₃, 150 MHz, ppm): δ = 7.89 (s, 2H), δ = 6.83-7.11 (br, 2H), δ = 3.84-4.20 (br, 4H), δ = 2.93-3.52 (m, 24H), δ = 1.73-2.22 (m, 10H). The molecular weight and polydispersity index (PDI) were determined by gel permeation chromatography (GPC) with DMF as eluent and polystyrene as standard substance: Mw = 11628, Mn = 9185, PDI =1.3.
Fig. S1. $^1$H NMR spectrum of tributyl(thiophen-2-yl)stannane.

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Fig. S4. $^{13}$C NMR spectrum of NDI-NN.
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Fig. S6. (a) Molecular structure of PNDI-C20. (b) ESR spectra of PNDI-NN, PNDI-C20 in film state.

Fig. S7. (a) $J-V$ curves and (b) PCE distributions of OSCs with different concentrations of PNDI-
Table. S1. Photovoltaic parameters of OSCs with different concentrations of PNDI-NN. (The average values in brackets are calculated from 16 devices.)

<table>
<thead>
<tr>
<th>ETM</th>
<th>C (mg/mL)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$FF$ (%)</th>
<th>Efficiency (%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>(0.836 ± 0.007)</td>
<td>(25.26 ± 0.37)</td>
<td>(69.41 ± 0.84)</td>
<td>(14.65 ± 0.10)</td>
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<tr>
<td>0.5</td>
<td>0.844</td>
<td>25.50</td>
<td>69.64</td>
<td>14.72</td>
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<tr>
<td></td>
<td></td>
<td>(0.845 ± 0.005)</td>
<td>(25.75 ± 0.57)</td>
<td>(70.24 ± 1.13)</td>
<td>(15.33 ± 0.21)</td>
</tr>
<tr>
<td>PNDI-NN</td>
<td>1</td>
<td>0.840</td>
<td>26.32</td>
<td>71.64</td>
<td>15.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.840 ± 0.003)</td>
<td>(25.66 ± 0.45)</td>
<td>(68.62 ± 0.52)</td>
<td>(14.79 ± 0.22)</td>
</tr>
<tr>
<td>2</td>
<td>0.842</td>
<td>25.48</td>
<td>69.56</td>
<td>14.93</td>
<td></td>
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</table>

Fig. S8. Box charts of photovoltaic parameters of (a) $V_{oc}$, (b) $J_{sc}$, (c) $FF$ and, (d) PCE extracted from $J-V$ measurements for the devices with and without PNDI-NN as ETLs.
Fig. S9. $J^{1/2}$-$V$ curves of the electron-only devices (ITO/Al/PM6:Y6/PNDI-NN/Ag). The electron mobility ($\mu_e$) was extracted by fitting data according to the space charge limited current (SCLC) model (Fig. 1(c)). The $\mu_e$ of PNDI-NN obtained by this method is $4.18 \times 10^{-4}$ cm$^2$ V$^{-1}$ S$^{-1}$ ($J=9/8[\varepsilon_r \varepsilon_0 \mu_e (V_{2 eff}/L^3)]$, here $J$ is current density, $\varepsilon_0$ is vacuum dielectric constant, $\varepsilon_r$ is relative dielectric constant, $L$ is film thickness, $V$ is effective voltage).

Table. S2. Electron mobilities of the electron-only devices with and without PNDI-NN.

<table>
<thead>
<tr>
<th>Interlayer</th>
<th>None</th>
<th>PNDI-NN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron mobility ($\mu_e$, cm$^{-2}$ V$^{-1}$ s$^{-1}$)</td>
<td>$3.54 \times 10^{-4}$</td>
<td>$4.76 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Fig. S10. (a) The stability of the OSCs devices with different electron transport materials in air with a relative humidity of 28%, (b) thermal stability of the devices at 85 °C.