Supporting Information

Naphthalene Diimide and Benzothiadiazole Copolymer Acceptor for All-Polymer Solar Cells with High Open-Circuit Voltage
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1. Measurements of Electrochemical Cyclic Voltammetry:

The electrochemical cyclic voltammetry (CV) was conducted with Pt disk, Pt plate, and Ag/AgCl electrode as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) acetonitrile solution. The polymer films were coated on a glassy carbon electrode from a DCB solution of polymer (~4 mg/mL). The potential of Ag/AgCl electrode is located at 4.4 eV. The energy levels of the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) were then calculated according to the equations:

\[ E_{\text{LUMO}} = -e(E_{\text{red}} + 4.4) \text{ (eV)} \]

\[ E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.4) \text{ (eV)} , \]

where \( E_{\text{red}} \) is the onset reduction potential vs Ag/AgCl, and \( E_{\text{ox}} \) is the onset oxidation potential vs Ag/AgCl.

2. Measurements of the charge mobility by the space-charge limited current (SCLC) method:

The hole mobility were carried out using the space charge limited current method (SCLC), employing a device architecture of ITO/PEDOT:PSS(30nm)/ PBDT-TT:polymer (~100 nm for PNDIBTH and ~120 nm for PNDIBTOC8) /Au(600nm) and ITO/TIPD (30nm)/PBDT-TT:polymer(~100 nm for PNDIBTH and ~120 nm for PNDIBTOC8)/Au(600nm) for the hole and electron mobility, respectively. The active layers were spin-coated under the conditions that afford the best photovoltaic results. The following equation was applied to estimate the hole and electron mobilities:

\[ J = \frac{9}{8}\varepsilon\mu_hV^2/L^3\exp\left[0.89\left(V/E_0L\right)^{0.5}\right] \]

where \( \varepsilon \) is the average dielectric constant of the blended film (here, \( \varepsilon \) is taken as 3.0 typically for polymers), the permittivity of the vacuum, \( \mu_h \) the zero-field mobility, \( E_0 \) the characteristic field, \( J \) the current density, \( L \) the thickness of the films, and \( V = V_{\text{appl}} - V_{\text{bi}}; V_{\text{appl}} \) the applied potential, and \( V_{\text{bi}} \) the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, \( V_{\text{bi}} = 0.2 \text{ V} \)). The results are plotted as \( \ln(JL^3/V^2) \) vs \( (V/L)^{0.5} \). The charge mobility of the blending films was deduced from the intercept value of \( \ln(9\varepsilon\mu_h\mu_0/8) \).

3. GPC results of PNDIBTH and PNDIBTOC8
4. Thermogravimetric properties of PNDIBTH and PNDIBTOC8
Fig. S2 TGA plots of PNDIBTH and PNDIBTOC8 with a heating rate of 10 °C/min under N\textsubscript{2} atmosphere.
5. DFT Calculation

**Fig. S3** DFT-calculated (B3LYP/6-31G(d)) molecular geometries and molecular orbitals of the trimmers of NDIBTH and NDIBTOC8.

<table>
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<th>Molecules</th>
<th>Methods</th>
<th>LUMO (eV)</th>
<th>HOMO (eV)</th>
<th>$E_g$ (eV)</th>
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**Table S1.** The electrochemical data of PNDIBTH and PNDIBTOC8 calculated from DFT calculation and cyclic voltammograms.
6. Mobility measurement.

Fig. S4. Plots of $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$ of blend films based on PNDIBTH and PNDIBTOC8 processed with 1% DIO. Hole mobility and electron mobility characteristics extracted from the hole-only SCLC curves and electron-only SCLC devices in optimal conditions.


Fig. S5. Out-of-plane grazing incidence X-ray scattering pattern of both polymer films in pure films (a) and blend films (b). Pure films were spin-coated on PEDOT:PSS/Si substrates.