Electronic Supplementary Information

Ambipolar Field-Effect Transistors Using Conjugated Polymers with the Structures of Bilayer, Binary Blends, and Paralleled Nanofibers†

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Experimental

Materials

Poly(3-hexylthiophene) (P3HT) ($M_w=50\,000$, 90-95% regioregularity) was used as received from Reike Metals Inc. (Lincoln, NE). P(NDI-T) was synthesized under Stille coupling with moderate to molecular weights ($M_w \sim 39500$, PDI=1.84). PMMA ($M_w \sim 350\,000$) was purchased from Sigma-Aldrich (Milwaukee, WI). Tetrabutylammonium perchlorate (TBAP, TCI (Tokyo, Japan)) and octadecyltrichlorosilane (ODTS, Sigma-Aldrich) were used as received without further purification. Chlorobenzene (CB; anhydrous 99.8%) was purchased from Sigma-Aldrich.

Fabrication of Binary blend thin film and bilayer structure

The semiconductor blend of P(NDI-T) and P3HT (typically in the proportion of 1 : 1 by weight) was spin-casted onto the silicon wafer from a chlorobenzene (CB) solution (10mg/ml) at 1000 r.p.m for 60 sec. The bilayer transistor containing the P3HT and P(NDI-T) were fabricated through the method reported by Prof. Meng in 2006.¹ Spin-coat in the order of P3HT, new liquid buffer layer (1,2-propylene glycol), and P(NDI-T) layers. The film of P3HT and P(NDI-T) (both 10 mg/ml)were spin-coated at 1000r.p.m for 60 s. And the residual 1,2-propylene glycol were removed in the following baking process in vacuum due to its high viscosity at 0 °C (248 η/mPa s) and suitable boiling point (188 °C). The buffer-layer method could successfully prevent the dissolution between solution-processed polymer layers.

Electrospinning (ES) Process

A two-fluid coaxial electrospin system²³ containing core and shell precursor solutions in separated syringes was employed to produce the electrospun nanofibers on a modified collector. Each syringe was connected to a separate needle, and the needle was placed one inside the other to form a two-fluid coaxial electrospin system. 50 mg/mL of P3HT or 40 mg/ml of P(NDI-T) as core solution was dissolved in anhydrous chlorobenzene (CB) overnight under N₂-filled glovebox. 300 mg/mL of PMMA as shell
solution was dissolved in anhydrous CB with 10 wt % of TBAP added to increase conductivity and stabilize the cone-jet.\textsuperscript{4, 5} The two solutions were fed into the coaxial capillaries by two syringe pumps (KD Scientific Model 100, USA). The optimized feed rate of P3HT solution (core flow) was fixed at 0.1, 0.2, 0.3 mL/h and P(NDI-T) solution (core flow) was fixed at 0.1 mL/h while the feed rates of PMMA solution (shell flow) was operated at 1.0 mL/h. One highly aligned coaxial P3HT (core)/PMMA (shell) nanofiber and one highly aligned coaxial P(NDI-T) (core)/PMMA (shell) nanofiber individually and then transferred from collector to the silicon wafer with thickness 100 nm of SiO\textsubscript{2} with ODTS-modified at surface used as a gate dielectric. By rinsing the devices with acetone, PMMA shell was selectively removed from both the P3HT and P(NDI-T) fiber. The tip of the core needle was connected to a high-voltage power supply (chargemaster CH30P SIMCO, USA). The spinning voltage was set at 9.2-9.6 kV. The collector made of electrically charged conductive aluminum disk with a rectangular hole was placed 13 cm below the tip of the needle (working distance) to collect the aligned nanofibers, similar to our previous report\textsuperscript{4, 5} and the other literature.\textsuperscript{6} The fiber alignment could be controlled by not only the electrostatic force between positive-charged fibers and negative charge of gap edge stretching the fibers across the gap but also the electrostatic repulsion between the deposited and upcoming fiber further enhancing the parallel alignment. All experiments were carried out under ambient environment. The nanofibers were characterized by grazing incidence wide-angle X-ray diffraction patterns (GIXD) conducted on beamline BL17A1 in the National Synchrotron Radiation Research Center (NSRRC), Taiwan. X-ray diffraction (XRD) was performed by X’Pert PRO X-ray diffractometer using Cu-Ka radiation ($\lambda = 1.321579$ Å) with a scan range typically of 0-25°, 0.014° per step. And the fiber morphology and size were also characterized by field-emission scanning electron microscope FE-SEM (JEOL JSM-6330F) with a 10 kV accelerating voltage and Leica DM4000M optical microscope.

**Device fabrication and electrical measurements**

Bottom gate/top contact FETs (see Fig. S1) were fabricated using a heavily doped silicon wafer
as the gate electrode with a 100 nm thick layer of thermally grown SiO₂ functioning as the gate dielectric (capacitance=30 nF/cm²). The source and drain electrodes consist of 100 nm of Au. An interdigital electrode configuration with typical length \( L = 0.1 \) mm and width \( W = 1 \) mm was used. The silicon oxide surface was treated with ODTS (octadecyltrichlorosilane) to form a hydrophobic monolayer coating following a procedure reported previously. To calculate the electrical properties of thin film transistors, in the saturation region \((V_d > V_g - V_t)\), \( I_d \) can be described by the following equation:\(^7\)

\[
I_{ds} = \frac{WC_o \mu}{2L}(V_g - V_t)^2
\]

where \( W \) and \( L \) are channel width and length, respectively, \( C_o \) is the capacitance of gate insulator per unit area (SiO₂, 100 nm, \( C_o = 25 \) nF/cm²), \( \mu \) is the hole mobility, and \( V_t \) is threshold voltage. The saturation region mobility of the studied conjugated materials is calculated from the transfer characteristics of OFET involving plotting \((I_d)^{1/2} \) versus \( V \). For the nanofiber transistors, in the saturation region, the modified equation for the current,

\[
I_{ds} = \mu \left( \frac{C}{L^2} \right)(V_g - V_t)^2
\]

was used to obtain the charge mobility because a semiconducting cylinder over a planar dielectric layer can be approximated by a coaxial capacitor for nanofiber based OFET devices.\(^8\) The capacitance per unit length (C/L) with respect to the back gate is described by \( 2\pi \varepsilon \varepsilon_o / \ln(2h/r) \), where \( r \), \( h \), and \( \varepsilon \) are the radius of the fiber, the thickness (100 nm) and average dielectric constant (~2.5) of SiO₂ dielectric layer, respectively.
References


Fig. S1 (a) GIXD pattern of electrospun nanofibers of P(NDI-T). (b) Optical microscopy image of P3HT and P(NDI-T) fibers across gold electrodes.
Fig. S2. Output characteristics of the ambipolar transistor in (a) bilayer, (b) binary blends, and (c) paralleled nanofibers FETs.
Fig. S3. (a) Optical image of complementary inverter. SEM images of the (b) p-type and (c) n-type fibers with gold electrode.
Fig. S4. (a) Transfer characteristics and (b) Voltage transfer characteristics of two-channel inverters with different diameter of P3HT nanofibers and P(NDI-T) nanofibers.