Enhanced near-infrared photoresponse of organic phototransistors based on single-component donor-acceptor conjugated polymer nanowires

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A conjugated polymer (PBIBDF-TT, Scheme S1) by introducing the solubilizing alkyl chain grafted bithiophene unit as the donor and the BIBDF unit as the acceptor was synthesized.

**EXPERIMENTAL SECTION**

**Materials:** 6-Bromoindoline-2, 3-dione was obtained from Darui Chemical Co. Ltd., Shanghai, China. Other chemicals used in this work were purchased from Sigma-Aldrich Chemical Company, Alfa Aesar Chemical Company and Sinopharm Chemical Reagent Co. Ltd., China. Chemical regents were purchased and used as received. Tetrahydrofuran (THF) and toluene were freshly distilled over sodium wire under nitrogen prior to use. 5,5′-bis(trimethylstannyl)-4,4′-bis(dodecyl)-2,2′-bithiophene was synthesized via published procedures.¹

**Synthesis of BIBDF:** The BIBDF monomer was synthesized via the procedures reported in our previous work.²

**Synthesis of 5,5′-bis(trimethylstannyl)-4,4′-bis(dodecyl)-2,2′-bithiophene:**
The 5,5′-bis(trimethylstannyl)-4,4′-bis(dodecyl)-2,2′-bithiophene monomer was synthesized via the procedures reported in previous work.3 A solution of n-butyllithium (6.13 mL, 12.27 mmol, 2 M in hexane) was added slowly to 4,4′-bis(dodecyl)-2,2′-bithiophene (2.8 g, 15.58 mmol) in tetrahydrofuran (60 mL) at −78 °C. After addition, the mixture was stirred for 30 min at room temperature. The mixture was cooled to −78 °C again. Trimethyltin chloride solution (12.27 mL, 12.27 mmol, 1.0 M in hexane) was added to the mixture, stirred for 30 min at −78 °C, then warmed to room temperature and was stirred overnight. The reaction was quenched with addition of water (150 mL) and the mixture was extracted with diethyl ether for three times. The combined organic layer was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by recrystallization in iso-propanol to afford a light yellow solid (1.87 g, 40.4%). 1H NMR (400 MHz, CDCl3, ppm): δ 7.10 (s, 2H), 2.54 (t, 4H), 1.58 (m, 4H), 1.26 (m, 36H), 0.88 (t, 6H), 0.37 (s, 18H).

Synthesis of polymer PBIBDF-TT: Tris(dibenzylideneacetone)dipalladium (Pd2(dba)3, 0.006 g, 0.0082 mmol), tri(o-tolyl)phosphine (P(o-tol)3, 0.008 g, 0.025 mmol) were added to a solution of 5,5′-bis(trimethylstannyl)-4,4′-bis(dodecyl)-2,2′-bithiophene (0.13 g, 0.16 mmol) and BIBDF (0.20 g, 0.16 mmol) in toluene (6 mL) under nitrogen. The solution was subjected to three cycles of evacuation and admission of nitrogen. The mixture was then heated to 110 °C for 48 h. After cooled to room temperature, the mixture was poured into methanol and stirred for 2 h. A black precipitate was collected by filtration. The product was purified by washing with methanol and petroleum ether in a Soxhlet extractor for 24 each. It was extracted with hot chloroform in an extractor for 24 h. After removing solvent, a black solid was collected (0.19 g, 76%). 1H NMR (400 MHz, CDCl3), σ (ppm): 9.0-9.15 (br, 4H), 6.85-7.20 (br, 6H), 3.65-3.75 (br, 4H), 2.50-2.70 (br, 4H), 0.95-1.95 (br, 72H) 0.65-0.95 (br, 18H). Molecular weights of all polymers were determined by gel-permeation chromatography (GPC) with 1,2,4-trichlorobenzene (TCB) as an eluent at 100 °C: Mn=19.4kDa (PDI= 1.98). Elemental Analysis: calcd for (C106H160N2O6S2)n (%): C, 78.47, H, 9.94, N, 1.73,
Characterization: Nuclear magnetic resonance (NMR) spectra were recorded on a Mercury plus 400 MHz machine. Gel permeation chromatography (GPC) analyses were performed on a Waters Series 1525 gel coupled with UV-vis detector using 1,2,4-trichlorobenzene as eluent with polystyrene as standards. Elemental analysis of the polymer was performed using a Vario EL instrument.

**Figure S1.** UV-vis-NIR absorption of PBIBDF-HH and PBIBDF-TT in solution and thin film.

**Figure S2.** SEM image of some defects formed on the nanowires during the
fabrication process

Figure S3. The transfer characteristics of PBIBDF-TT top-contact NW-OPTs under NIR illumination and in dark condition, (a) $V_{DS} = -80$ V, (b) $V_{DS} = 80$ V.

Figure S4. (a) Temperature variation curves of PBIBDF-TT NW-OPTs and CYTOP-treated thin-film OPTs upon NIR illumination with a light intensity density of 47.1 mW cm$^{-2}$ (b) Hole mobility enhancement of PBIBDF-TT NW-OPTs and CYTOP-treated thin-film OPTs with increasing temperatures.

The temperature variations of NW-OPTs and thin-film OPTs were measured using infrared imaging device under NIR illumination at a light intensity density of 47.1 mW cm$^{-2}$ in 40 seconds, which was longer than the test time. The devices were measured using probe station in such temperature variation range.
Reference