

Fluorinated benzothiadiazole and indacenodithieno[3,2-b]thiophene based regioregular-conjugated copolymers for ambipolar organic field-effect transistors and inverters

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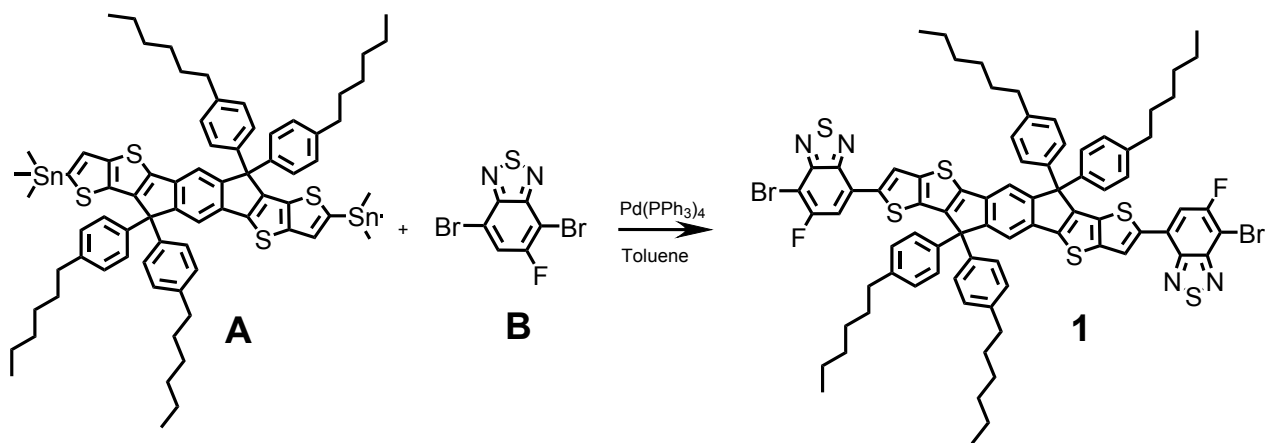
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Materials and characterization

Materials:

All starting materials and reagents were purchased from commercial supplies unless otherwise specified, and used without further purification. In particular, compounds indacenodithieno[3,2-b]thiophene (compound A, Solarmer Materials Inc.), 4,7-dibromo-5-fluoro-2,1,3-benzothiadiazole (compound B, Hanchem Co., Ltd.), 2,5-dihydro-2,5-dioctyl-3,6-bis[5-(trimethylstannyl)-2-thienyl]-Pyrrolo[3,4-c]pyrrole-1,4-dione (compound 2, Suna Tech Inc.) 2,6-Bis(trimethylstannyl)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (compound 3, Solarmer Materials Inc.), and 2,6-Bis(trimethylstannyl)-4,8-bis(5-(2-ethylhexyl)selenophene-2-yl)benzo[1,2-b:4,5-b']dithiophene (compound 4, Solarmer Materials Inc.) were purchased commercially.



Scheme S1. Synthetic route for monomer 1.

Synthesis

Preparation of compound 1: Compounds A (2.0 g, 1.49 mmol) and B (1.07 g, 3.42 mmol), toluene (50 ml) were mixed in a 100 ml round bottom flask, and tetrakis(triphenylphosphine)palladium Pd(PPh₃)₄ (50 mg) was mixed, then the reaction mixture was heated at 100°C for 24 h. The reaction was quenched with water, extracted with chloroform, and dried over MgSO₄. The solvent was then evaporated under vacuum and the crude product was purified by chromatography on silica gel (eluent: hexane/dichloromethane=2:1) to obtain the desired product (72% yield). ¹H NMR (CDCl₃, 500 MHz, [ppm]): δ 8.60 (s, 2H), 7.62~7.65 (d, 2H), 7.57 (s, 2H), 7.22~7.23 (d, 8H), 7.12~7.14 (d, 8H), 2.55~2.59 (t, 8H), 1.56~1.61 (m, 8H), 1.26~1.35 (m, 24H), 0.84~0.87 (m, 12H); MS (MALDI-TOF): calculated C₈₀H₇₄Br₂F₂N₄S₆ m/z=1480.26; actual = 1478.3.

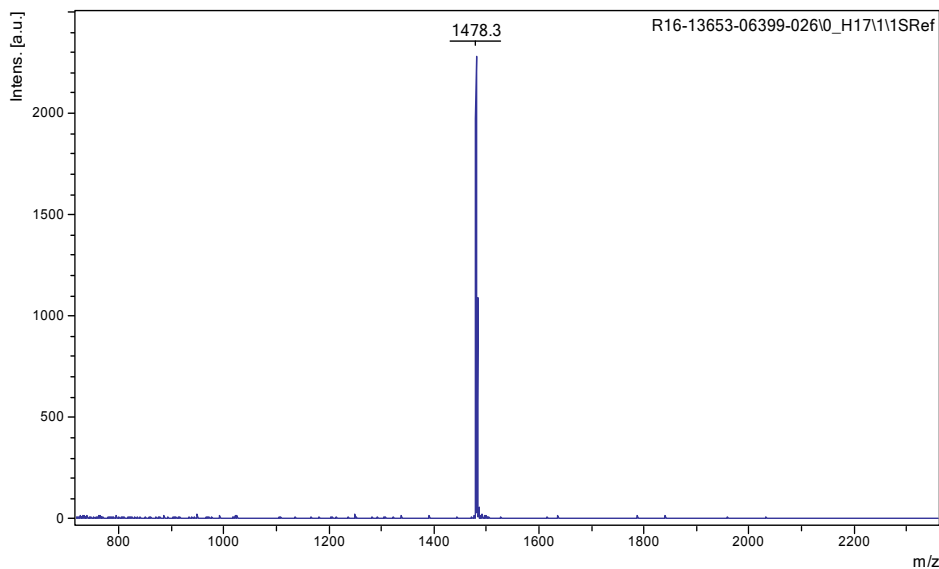


Fig. S1. MALDI-TOF Mass spectrum for compound 1

Characterization and measurements.

A microwave reactor (Biotage Initiator™) was used to synthesize the polymers. UV-vis spectra were obtained with a Mecasys Optizen Pop spectrophotometer. The numerical and weight averaged molecular weights of the polymers were determined by gel-permeation chromatography (GPC) with chlorobenzene eluent at 80°C using a Waters 1515 system, relative to polystyrene standards. Cyclic voltammetry (CV) measurements were performed with an AutoLab analyzer. All CV measurements were performed in 0.1 M tetrabutylammoniumtetrafluoroborate (Bu_4NBF_4) in acetonitrile with platinum as the counter electrode, 3 mm Glassy carbon coated with a thin polymer film as the working electrode, and Ag/Ag⁺ as the reference electrode.

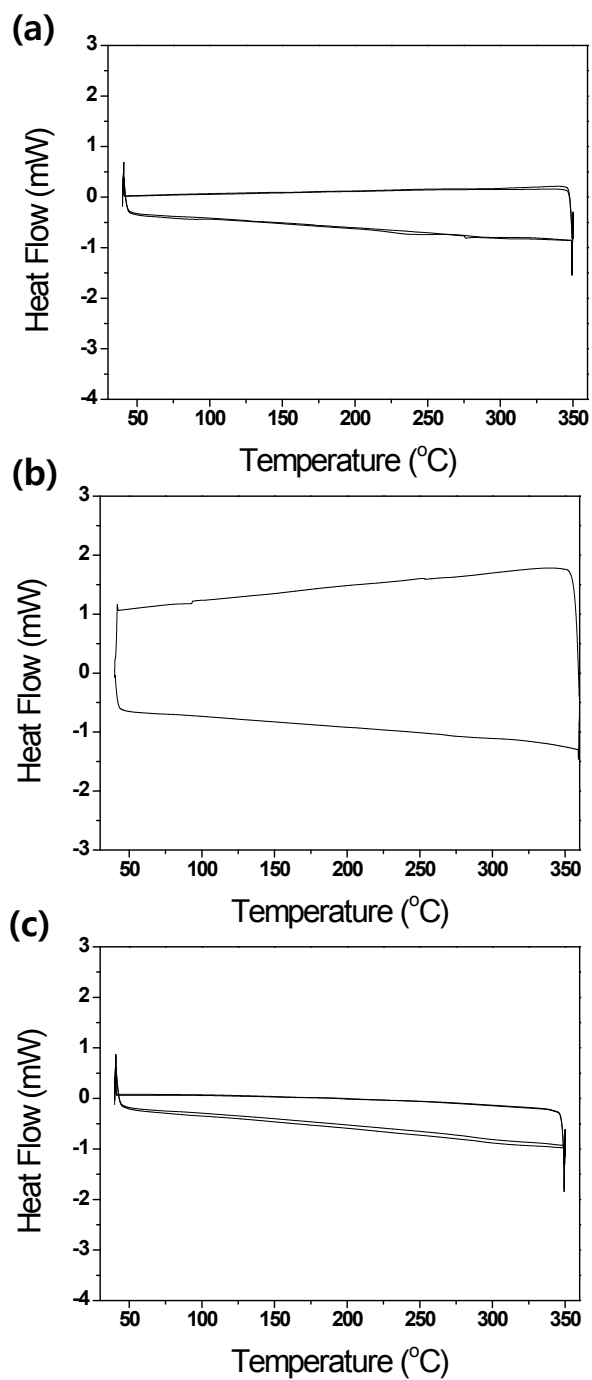


Fig. S2. DSC curves for (a) **P1**, (b) **P2**, and (c) **P3** polymers

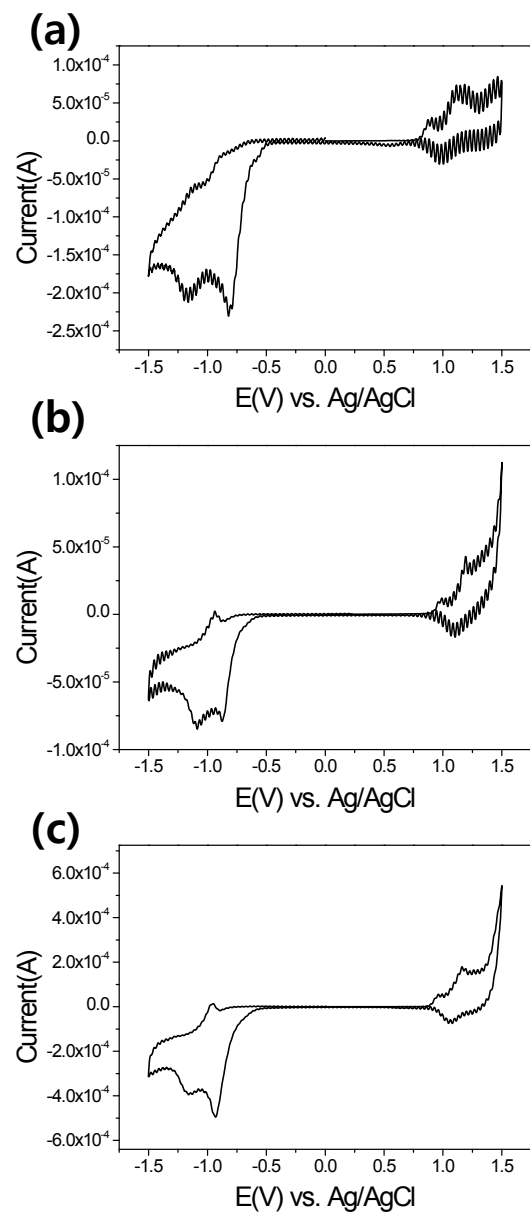


Fig. S3. Cyclic voltammograms of (a) **P1**, (b) **P2**, and (c) **P3** polymers

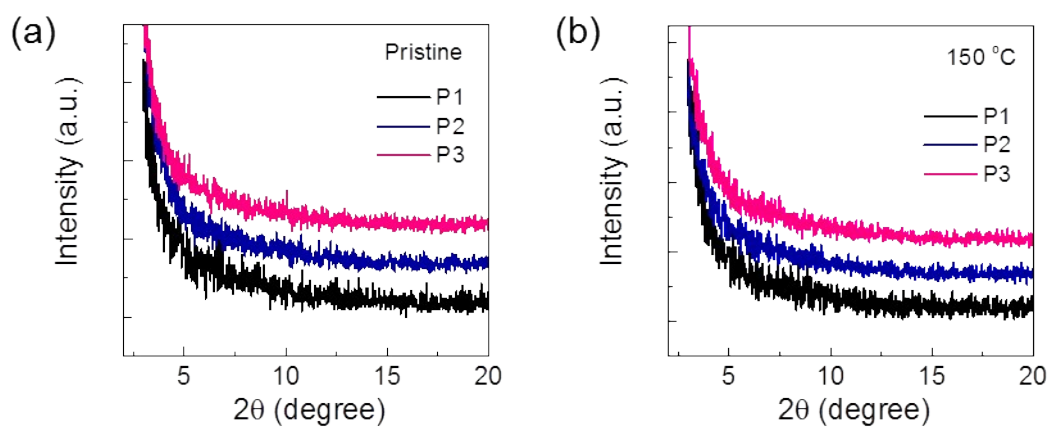


Fig. S4. X-Ray Diffraction spectra of (a) pristine and (b) 150°C annealed BT-IDTT based polymers.

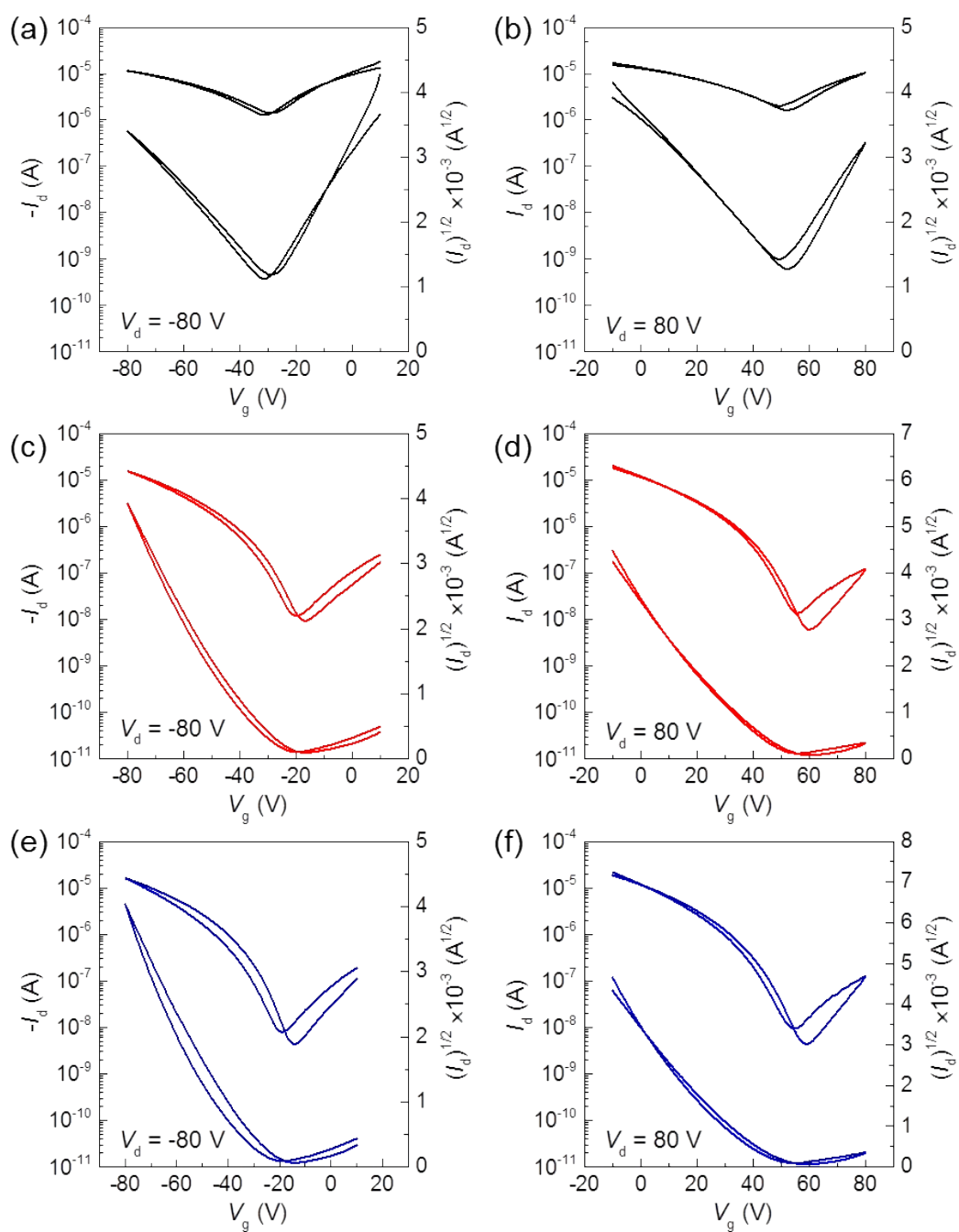


Fig. S5 Transfer characteristics of pristine **P1** OFETs in (a) p -channel and (b) n -channel; pristine **P2** OFETs in (c) p -channel and (d) n -channel; and pristine **P3** OFETs in (e) p -channel and (f) n -channel

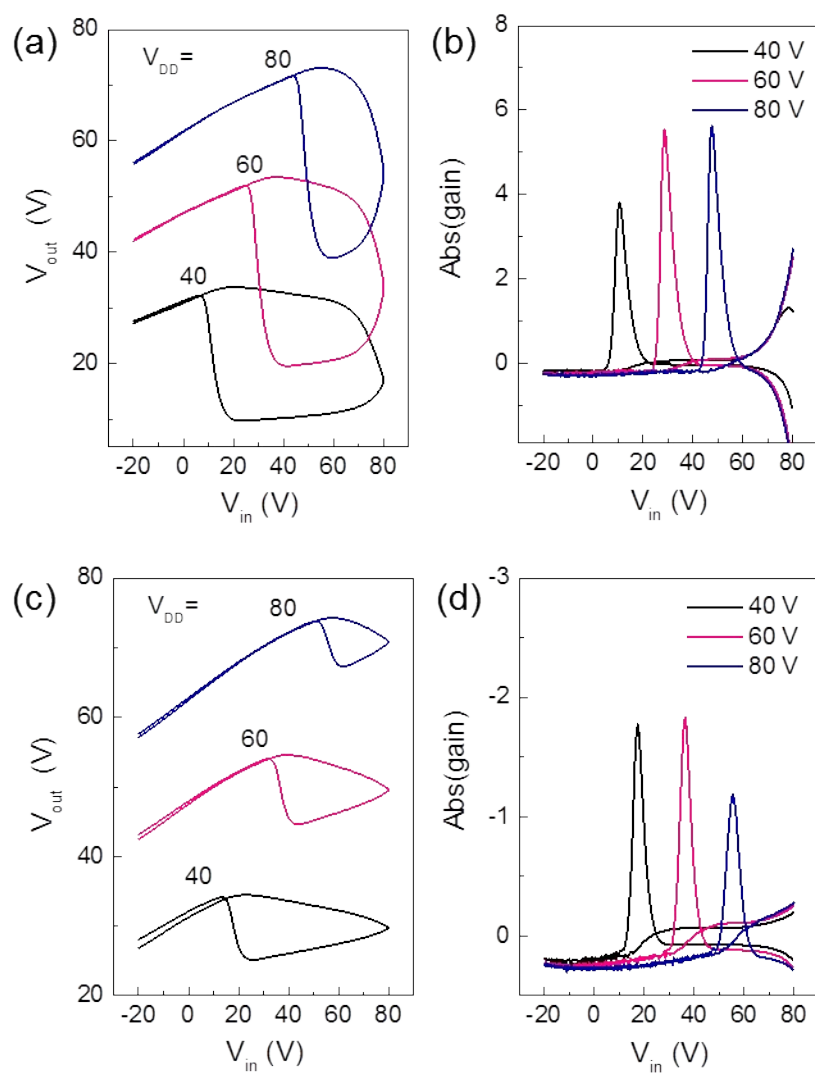


Fig. S6. (a), (c) Voltage transfer characteristics and (b), (d) corresponding voltage gains at various V_{DD} from 40–80 V for complementary inverter circuits based on **P2** and **P3** polymers, respectively