# **Electronic Supplementary Information**

# Thiophene backbone-based polymers with electron-withdrawing pendant groups for application in organic thin-film transistors

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## **Experimental details**

#### Materials

5,5'-bis(trimethylstannyl)-2,2'-bithiophene, tetrakis(triphenylphosphine)palladium(0), tris(dibenzylideneacetone)dipalladium(0), and all the solvents were purchased from Sigma-Aldrich. Tri(o-tolyl)phosphine was provided by Alfa Aesar. 1,3-Dibromo-5,7-bis(2-butyloctyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c*']dithiophene-4,8-dione was obtained from Suna Tech Inc. All the chemicals were used as received, without further purification.

### Characterization of materials

The <sup>1</sup>H nuclear magnetic resonance spectra were recorded at 25 °C with a Bruker Ascend TM-400 spectrometer. The absorption spectra were measured by a Shimadzu UV-2550 UV–visible spectrophotometer. The cyclic voltammetry measurments were conducted at a scan rate of 30 mV/s by using a BASi 100B/W electrochemical analyzer with a three-electrode cell and a 0.1 N Bu<sub>4</sub>NBF<sub>4</sub> solution in acetonitrile as the electrolyte; the working electrode was coated with the polymer films by dipping into their solutions in chloroform. All the measurements were calibrated against an internal standard of ferrocene (Fc), whose ionization potential is -4.8 eV for the Fc/Fc<sup>+</sup> redox system. The gel permeation chromatography analysis was conducted with a Waters Breeze 2 system at room temperature by using chloroform as the eluent.

Temperature-dependent absorption spectra of PF2-BDD and PT2-BDD were measured via preparing the polymer solution at 80°C. The hot solution was slowly cooled to room temperature and the change in absorption was observed through the repeated measuremnt using UV–visible spectroscopy.



**Fig. S1**. Gel permeation chromatogram of poly[(2,2'-bithiophene-5,5'-diyl)-alt-(5,7-bis(2-butyloctyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione-1,3-diyl)] (PT2-BDD).



**Fig. S2**. Gel permeation chromatogram of poly[(3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)-alt-(5,7-bis(2-butyloctyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione-1,3-diyl)] (PF2-BDD).



**Fig.S3**. <sup>1</sup>H nuclear magnetic resonance spectrum of poly[(2,2'-bithiophene-5,5'-diyl)-alt-(5,7-bis(2-butyloctyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione-1,3-diyl)] (PT2-BDD).



**Fig. S4**. <sup>1</sup>H nuclear magnetic resonance spectrum of poly[(3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)-alt-(5,7-bis(2-butyloctyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione-1,3diyl)] (PF2-BDD).