Scheme S1. The synthetic route to SnA2: (i). LDA, THF, -78 °C; then -50°C, 1h; -78 °C, Me₃SnCl, room temperature.

Compound A2 was prepared according to the literature procedure.¹

**Compound SnA2.** Compound A2 (0.47 g) was dissolved in anhydrous THF (20 ml) under the protection of nitrogen. The solution was cooled to -78 °C and lithium diisopropylamine (LDA, 2 M, 2.5 ml) was added dropwise into the mixture. Then the reaction solution was warmed up to -50 °C and kept at the temperature for 2 hours. Finally the resulting mixture was cooled down to -78 °C again, and trimethyltin chloride (0.1 g, dissolved in 3 ml of THF) was added dropwise to the system. The cooling bath was removed and the mixture was stirred overnight at room temperature under nitrogen atmosphere. Water was added under vigorous stirring to quench the reaction. The mixture was extracted with EtOAc and the organic phase washed with water, dried over magnesium sulfate. After evaporation of the solvent, the reside was recrystallized in dichloromethane:ethanol (1:10) to obtain a red crystalline solid (0.47 g, 59%).¹¹H NMR (400 MHz, CDCl₃, δ ): 8.08 (t, J=3.6Hz, 2H), 7.82 (s, 2H), 2.68 (t, J=8.0 Hz, 4H), 1.72-1.66 (m,4H), 1.46-1.26( m, 12H), 0.90 (t, J=6.8 Hz, 6H), 0.43 (s, 18H).

¹³C NMR (100 MHz, CDCl₃, δ): 152.62, 151.99, 144.52, 134.48, 129.89, 125.77, 125.61, 33.03, 32.18, 31.80, 29.39, 22.64, 14.12, -7.80. MS (MALDI-TOF) m/z: calcd for C₃₂H₄₈N₂S₃Sn₂ 794.3; found: 794.1.
Figure S1. TGA plots of the copolymers with a heating rate of 10 °C/min under nitrogen.

Figure S2. Typical transfer characteristics of the FETs based on the copolymers: (a) PC1BT6, (b) PC2BT6, (c) PC6BT6, (d) PNC2C4BT6, (e) PC2BT.
**Figure S3.** X-ray diffraction patterns of polymer thin films.

**Figure S4.** AFM topography images (500 nm × 500 nm) of films cast from chlorobenzene solutions. RA: roughness average.
Figure S5. TEM images of the BHJ active layer films based on different polymers: (a) PC1BT6; (b) PC2BT6; (c) PC6BT6; (d) PNC2C4BT6; (e) PC2BT.

References: