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## **Supporting Information**

## Naphthobisthiazole Diimide-Based n-Type Polymer Semiconductors: Synthesis, π-stacking, Field-Effect Charge Transport, and All-Polymer Solar Cells

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Figure S1. <sup>1</sup>H NMR (500 MHz) spectrum of NBTDI dibromide (3) in CDCl<sub>3</sub>.



Figure S2. <sup>13</sup>C NMR (125 MHz) spectrum of NBTDI dibromide (3) in CDCl<sub>3</sub>.



Figure S3. <sup>1</sup>H NMR (500 MHz) spectrum of PNBTDIP in CDCl<sub>3</sub>.



**Figure S4**. <sup>1</sup>H NMR (500 MHz) spectrum of PNBTDIT in CDCl<sub>3</sub>.



Figure S5. <sup>1</sup>H NMR (500 MHz) spectrum of PNBTDIV in CDCl<sub>3</sub>.



Figure S6. TGA thermograms of PNBTDIs in  $N_2$  obtained at a 10 °C min<sup>-1</sup> heating rate.



**Figure S7.** DSC scans of PNBTDIs at a heating/cooling rate of 10 °C min<sup>-1</sup> in nitrogen.



Figure S8. Output (a & c) and transfer (b & d) characteristics of PNBTDIT and PNBTDIP OFETs.



**Figure S9**. AFM topographical images (5 x 5  $\mu$ m<sup>2</sup>) of the surfaces of poly(naphthobisthiazole diimide)s and PSEHTT:PNBTDI blends: (a) PNBTDIP, (b) PNBTDIT, and (c) PNBTDIV; and their corresponding blend images of (d) PSEHTT:PNBTDIP, (e) PSEHTT:PNBTDIT and (f) PSEHTT:PNBTDIV.