

Electronic Supplementary Information

## Use of Heteroaromatic Spacers in Isoindigo-Benzothiadiazole Polymers for Ambipolar Charge Transport

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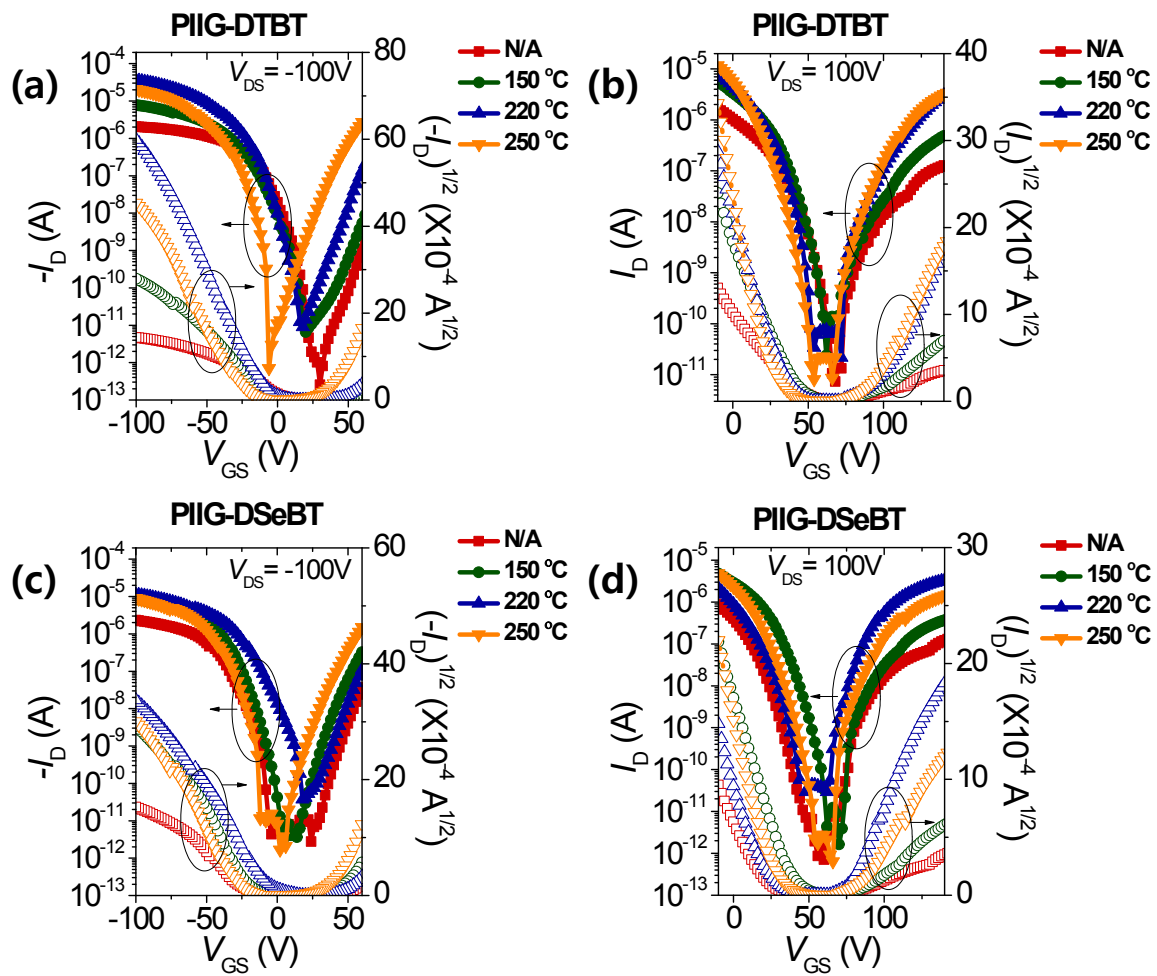
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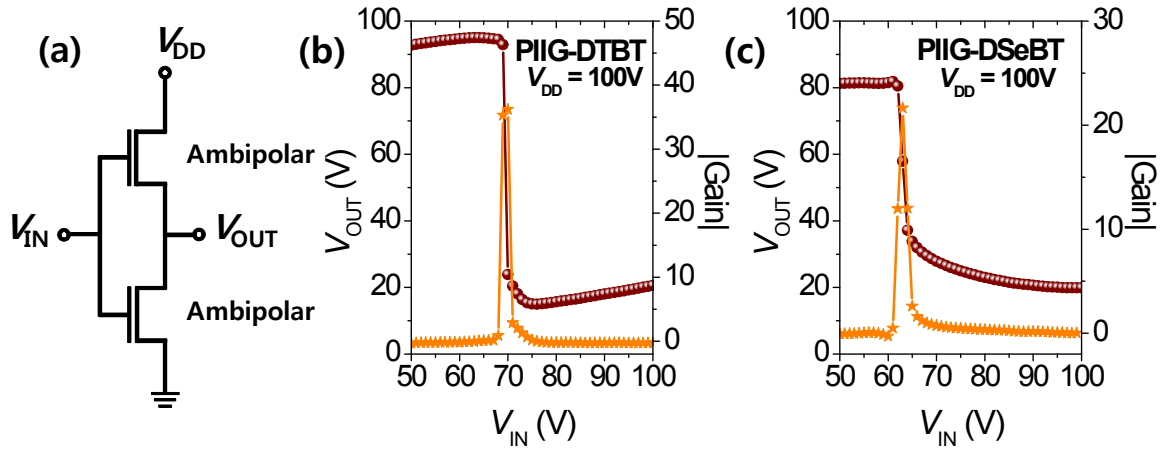


**Figure S1** Ambipolar charge-transport characteristics of spacer containing IIG-BT polymers depending on annealing temperature: {(a),(b)} **PIIG-DTBT** and {(c),(d)} **PIIG-DSeBT**. The ambipolar transistor operating in {(a),(c)} hole- and {(b),(d)} electron-enhancement mode at  $|V_{DS}|=100V$ , respectively.

**Table S1** OFET performance of spacer containing IIG-BT polymers depending on annealing temperature

| Polymer <sup>a</sup> | Annealing temperature | <i>p</i> -channel                                                     |                                                                       |                  |              | <i>n</i> -channel                                                   |                                                                     |                  |              |
|----------------------|-----------------------|-----------------------------------------------------------------------|-----------------------------------------------------------------------|------------------|--------------|---------------------------------------------------------------------|---------------------------------------------------------------------|------------------|--------------|
|                      |                       | $\mu_{h,max}^c$<br>[cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] | $\mu_{h,avg}^d$<br>[cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] | $I_{on}/I_{off}$ | $V_T$<br>[V] | $\mu_{e,max}$<br>[cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] | $\mu_{e,avg}$<br>[cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] | $I_{on}/I_{off}$ | $V_T$<br>[V] |
| <b>PIIG-DTBT</b>     | N/A <sup>b</sup>      | 9.5×10 <sup>-3</sup>                                                  | 7.1×10 <sup>-3</sup><br>(±1.7×10 <sup>-3</sup> ) <sup>e</sup>         | >10 <sup>6</sup> | 7.5          | 1.2×10 <sup>-3</sup>                                                | 4.9×10 <sup>-4</sup><br>(±4.3×10 <sup>-4</sup> )                    | >10 <sup>4</sup> | 85.8         |
|                      | 150 °C                | 1.7×10 <sup>-2</sup>                                                  | 1.1×10 <sup>-2</sup><br>(±5.4×10 <sup>-3</sup> )                      | >10 <sup>7</sup> | -18.8        | 2.2×10 <sup>-3</sup>                                                | 1.4×10 <sup>-3</sup><br>(±6.7×10 <sup>-4</sup> )                    | >10 <sup>4</sup> | 93.3         |
|                      | 220 °C                | 7.8×10 <sup>-2</sup>                                                  | 4.3×10 <sup>-2</sup><br>(±1.9×10 <sup>-2</sup> )                      | >10 <sup>7</sup> | -22.8        | 3.4×10 <sup>-2</sup>                                                | 1.4×10 <sup>-2</sup><br>(±1.3×10 <sup>-2</sup> )                    | >10 <sup>5</sup> | 95.6         |
|                      | 250 °C                | 6.3×10 <sup>-2</sup>                                                  | 4.0×10 <sup>-2</sup><br>(±3.7×10 <sup>-2</sup> )                      | >10 <sup>8</sup> | -32.2        | 2.1×10 <sup>-2</sup>                                                | 1.0×10 <sup>-2</sup><br>(±8.2×10 <sup>-3</sup> )                    | >10 <sup>5</sup> | 93.4         |
| <b>PIIG-DSeBT</b>    | N/A                   | 9.6×10 <sup>-3</sup>                                                  | 6.4×10 <sup>-3</sup><br>(±1.3×10 <sup>-3</sup> )                      | >10 <sup>5</sup> | -23.8        | 4.0×10 <sup>-4</sup>                                                | 3.6×10 <sup>-4</sup><br>(±5.1×10 <sup>-5</sup> )                    | >10 <sup>5</sup> | 78.3         |
|                      | 150 °C                | 1.1×10 <sup>-2</sup>                                                  | 9.0×10 <sup>-3</sup><br>(±2.4×10 <sup>-3</sup> )                      | >10 <sup>6</sup> | -26.2        | 5.3×10 <sup>-4</sup>                                                | 4.5×10 <sup>-4</sup><br>(±6.9×10 <sup>-5</sup> )                    | >10 <sup>5</sup> | 86.5         |
|                      | 220 °C                | 2.6×10 <sup>-2</sup>                                                  | 2.0×10 <sup>-2</sup><br>(±4.8×10 <sup>-3</sup> )                      | >10 <sup>6</sup> | -20.9        | 1.5×10 <sup>-2</sup>                                                | 5.3×10 <sup>-3</sup><br>(±4.2×10 <sup>-3</sup> )                    | >10 <sup>4</sup> | 87.2         |
|                      | 250 °C                | 1.2×10 <sup>-2</sup>                                                  | 9.8×10 <sup>-3</sup><br>(±2.6×10 <sup>-3</sup> )                      | >10 <sup>7</sup> | -29.2        | 9.6×10 <sup>-3</sup>                                                | 5.0×10 <sup>-3</sup><br>(±3.6×10 <sup>-3</sup> )                    | >10 <sup>4</sup> | 86.4         |

<sup>a</sup>The FET performance of more than 10 devices was tested in a nitrogen atmosphere. <sup>b</sup>The polymer films were not annealed. <sup>c</sup>The maximum and <sup>d</sup>average mobility of the FET devices ( $L = 50 \mu\text{m}$  and  $W = 1000 \mu\text{m}$ ). <sup>e</sup>The standard deviation.



**Figure S2** (a) Schematic of the complementary inverter structure. CMOS-like inverter characteristics of (b) **PIIG-DTBT** and (c) **PIIG-DSeBT** inverter ( $V_{DD} = 100$  V).