

## Electronic Supplementary Information

### **Controlling Dominant Polarity and Ambipolarity of Thieno-Benzo-Isoindigo Polymers-Based Transistors: The Role of Face-on and Edge-on Population**

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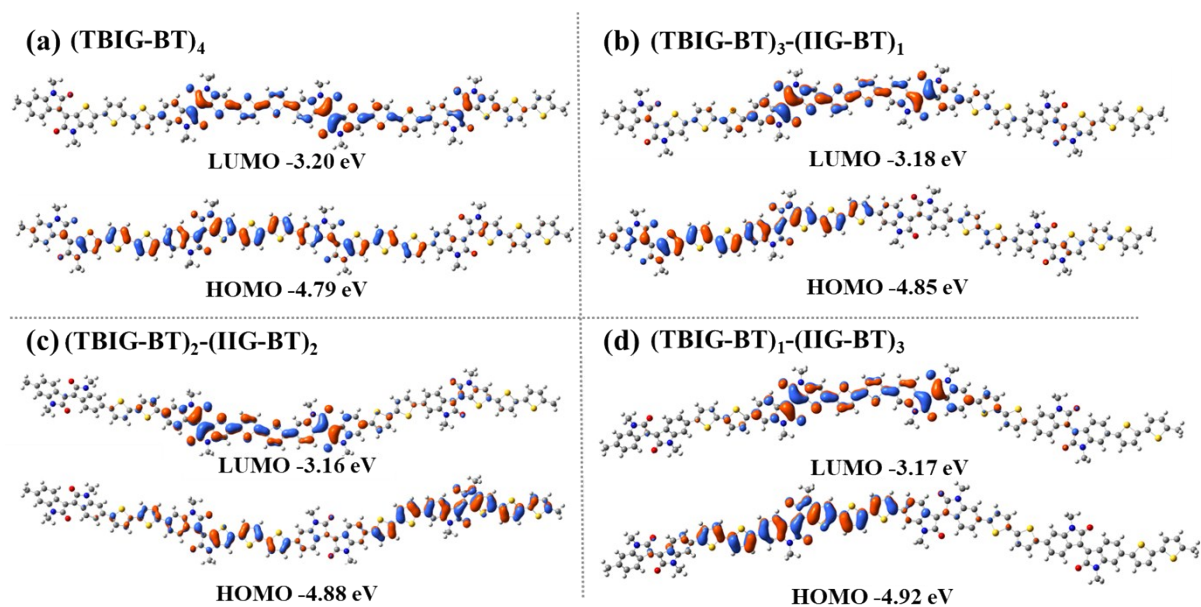
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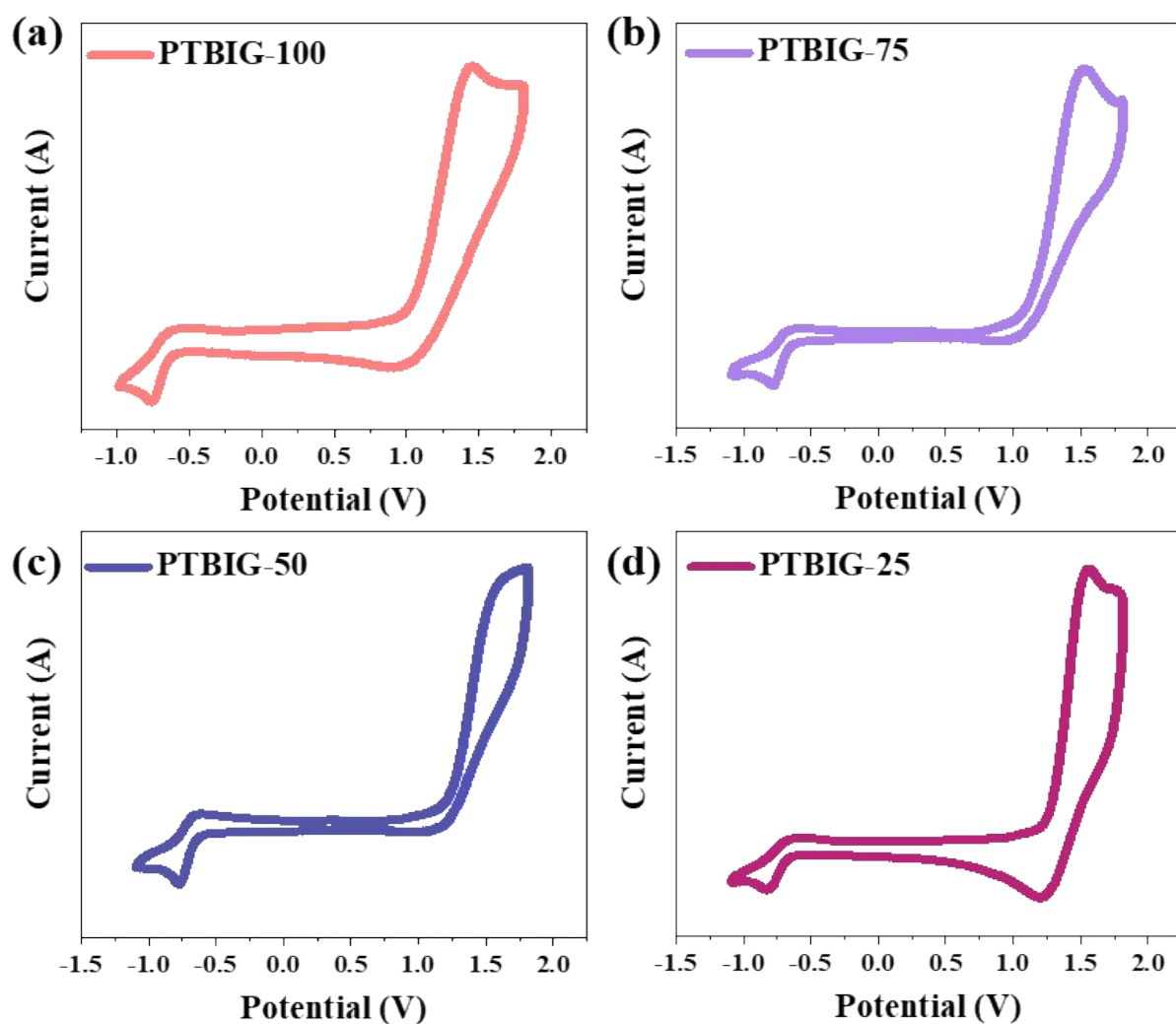
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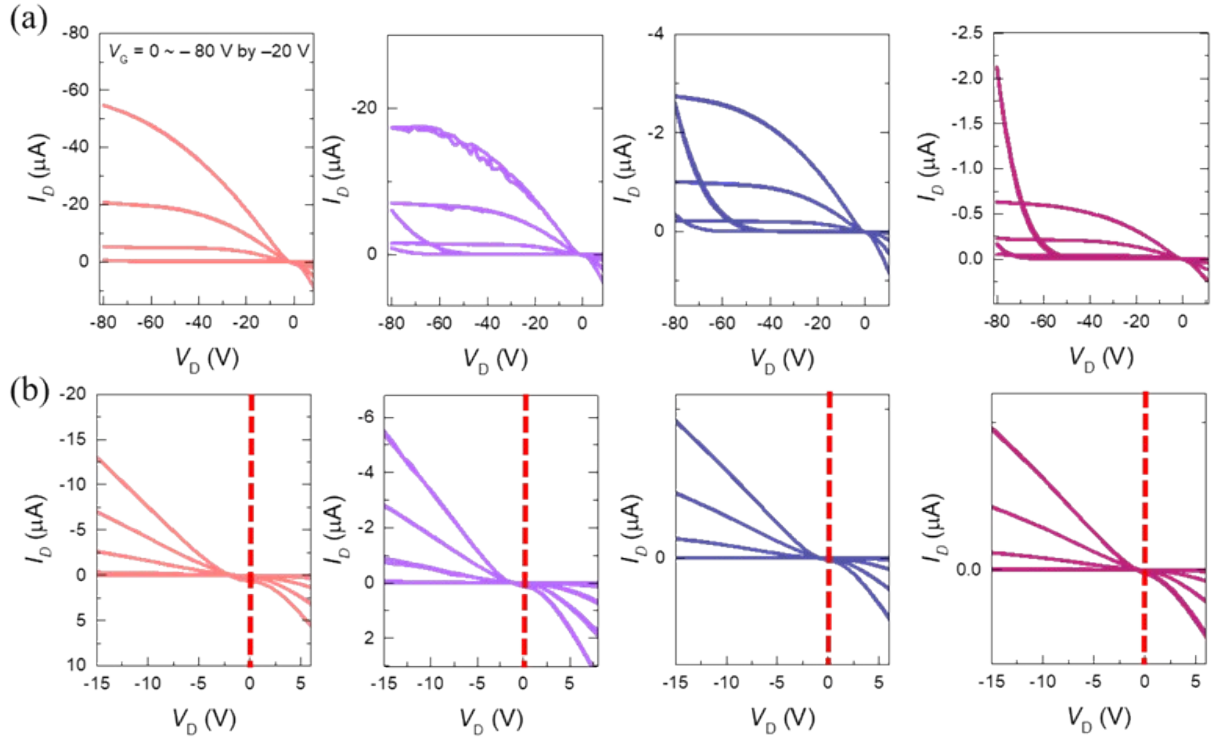
<sup>†</sup>These authors contributed to the work equally.



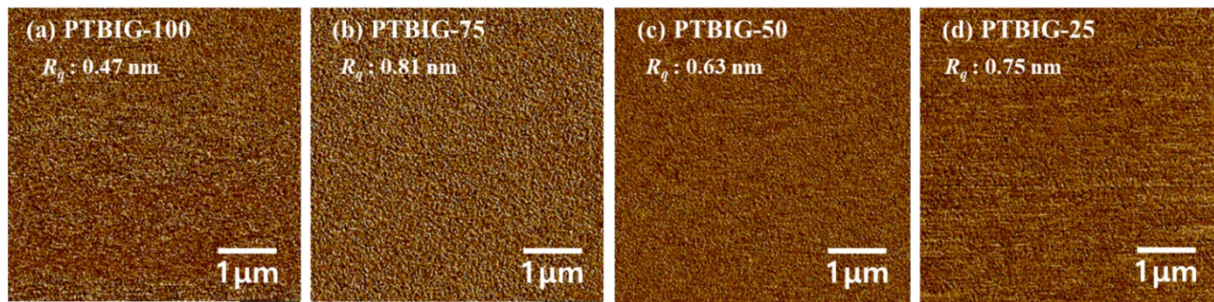
**Fig. S1** Optimized molecular geometries of tetramers of TBIG and IIG segments with calculated LUMOs and HOMOs of (a) (TBIG-BT)<sub>4</sub>, (b) (TBIG-BT)<sub>3</sub>-(IIG-BT)<sub>1</sub>, (c) (TBIG-BT)<sub>2</sub>-(IIG-BT)<sub>2</sub>, and (d) (TBIG-BT)<sub>1</sub>-(IIG-BT)<sub>3</sub>.



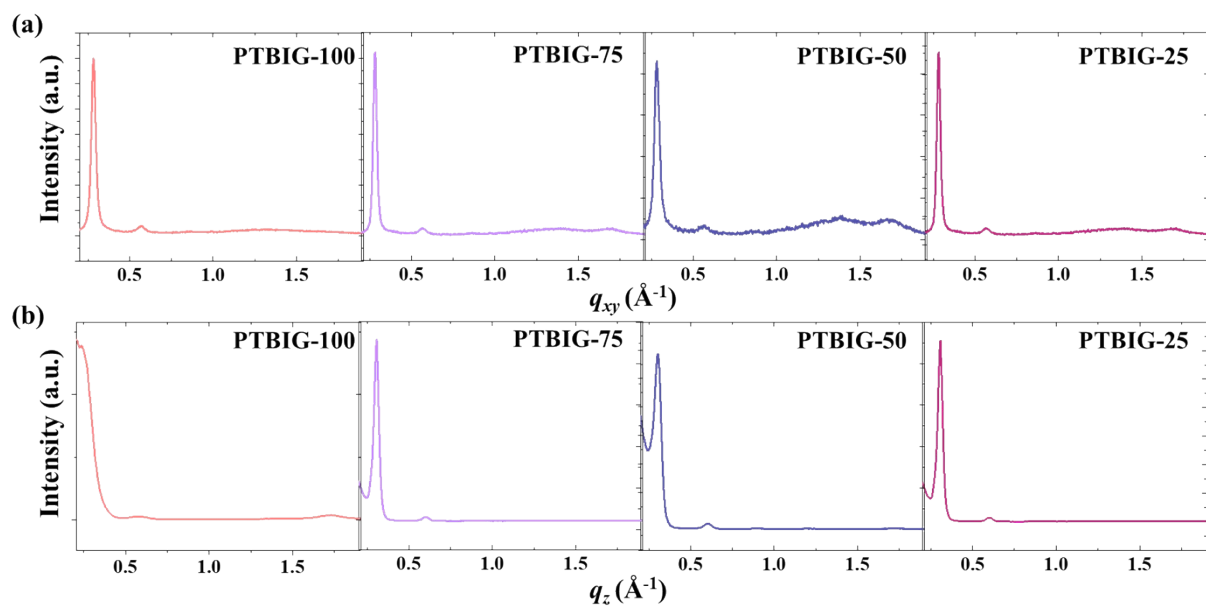
**Fig. S2** Cyclic voltammograms of (a) PTBIG-100, (b) PTBIG-75, (c) PTBIG-50, and (d) PTBIG-25.



**Fig. S3** (a) Output characteristics for TBIG:IIG OFETs with 100:0, 75:25, 50:50, and 25:75; (b) Enlarged figure of output curves in linear regime.



**Fig. S4** The AFM height images of (a) PTBIG-100, (b) PTBIG-75, (c) PTBIG-50, and (d) PTBIG-25.



**Fig. S5** 1-D profile for TBIG-based polymers films (a) in plane and (b) out of plane.