

# ADVANCED FUNCTIONAL MATERIALS

## Supporting Information

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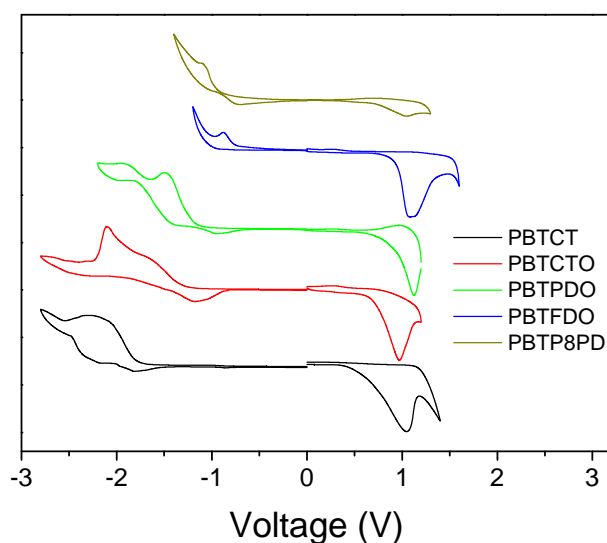
**Energy Level Modulation of HOMO, LUMO, and Band-Gap  
in Conjugated Polymers for Organic Photovoltaic  
Applications**

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W. Coir, Hossein Hashemi, Yoshio Aso, Peter F. Green, John  
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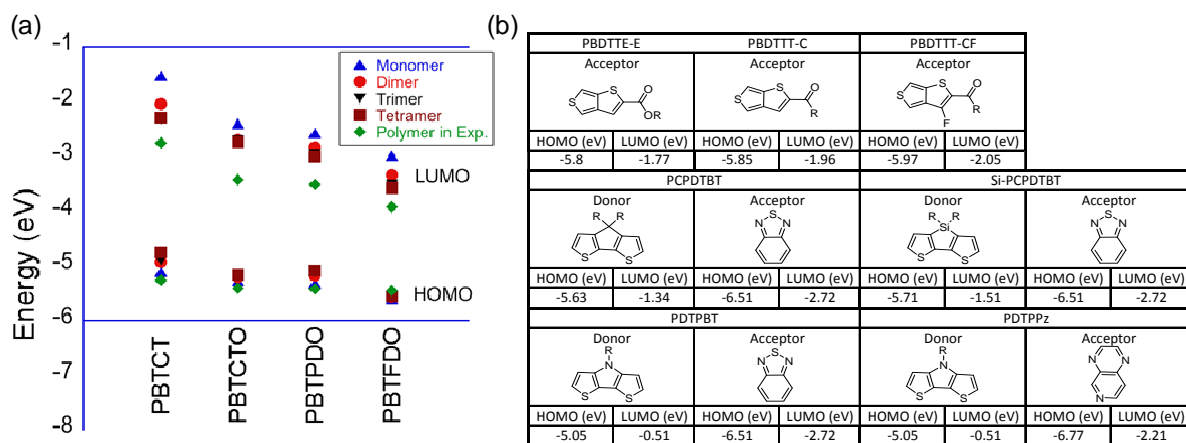
## Supporting Information

### Energy Level Modulation in Conjugated Polymers; HOMO, LUMO and Band-Gap for Organic Photovoltaic Application

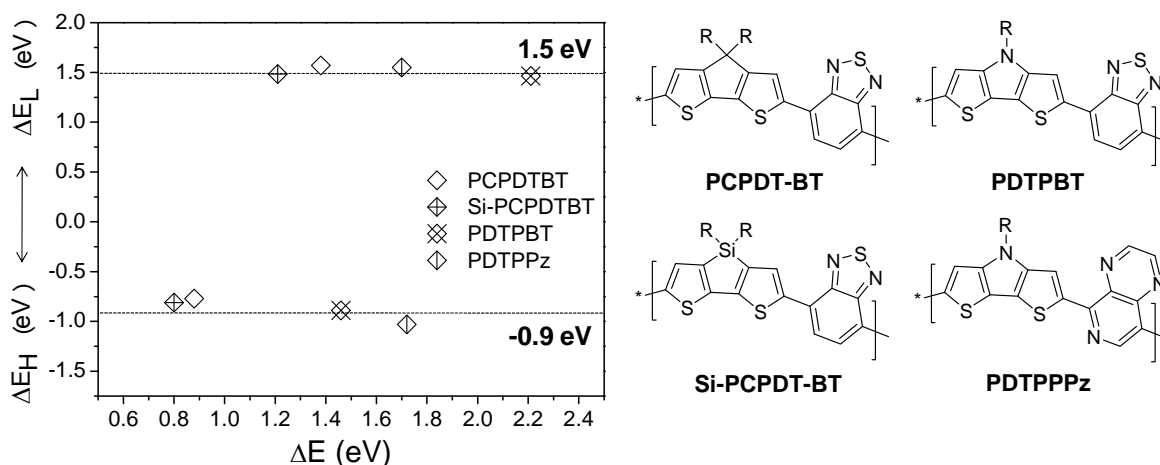
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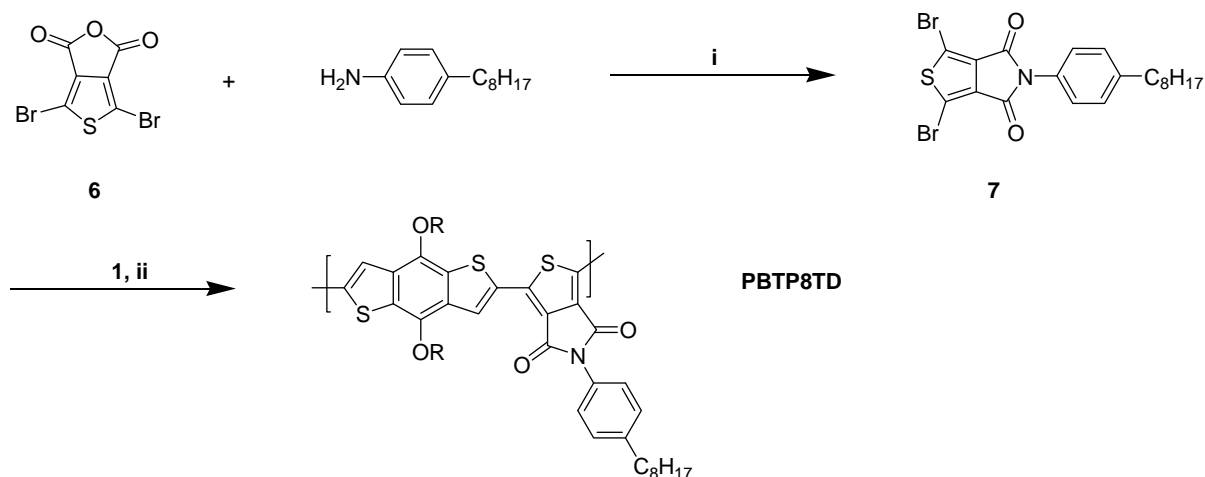
**Figure S1.** Oxidation and reduction potential of obtained CPs.



**Figure S2.** (a) Calculated energy level trend as increasing repeating unit, and (b) summary of applied monomers' energy levels obtained from the calculation. R was simplified as methyl for the calculation.



**Figure S3.** Analyzed energy level diagram with reported CPs sharing similar conformation.



**Scheme S1.** Detailed synthetic scheme of PBT8PT. R indicates 2-ethylhexyl group, i) and ii)  $\text{Pd}_2(\text{dba})_3$ ,  $\text{P}(\text{o-tolyl})_3$ , toluene,  $110^\circ\text{C}$ , 48 hours.

**Materials.** All starting materials were purchased from commercial supplier (Aldrich and Fisher Sci.). Synthesized compounds were fully characterized with  $^1\text{H-NMR}$  and GC-mass. Compound **1**, **2**, **3**, **4**, **5**, **6** were prepared as previously described manner.<sup>[1-5]</sup>

*1,3-dibromo-5-(4-octylphenyl)-5H-thieno[3,4-c]pyrrole-4,6-dione (7).* 4,6-dibromothieno-[3,4-c]furan-1,3-dione (**6**) (1.45 g, 4.67 mmol), 4-octylbenzenamine (0.47 ml, 2.07 mmol), and DMAP (0.69 g, 5.6 mmol) were dissolved into anhydrous dioxane (30 ml). Then, the mixture was stirred for 20 hr under  $55^\circ\text{C}$ . Acetic anhydride (17 ml) was added to the mixture and it was heated to  $80^\circ\text{C}$ . After additional stirring for 4 hr, the mixture was poured in to water and extracted with dichloromethane. The organic layer was collected and dried with  $\text{MgSO}_4$ . The product was obtained from column chromatography after evaporating solvent under vacuo.  $^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (d, 2H), 7.23 (d, 2H), 2.63 (t, 2H), 1.62 (m, 2H), 1.36 – 1.29 (m, 10H), 0.88 (t, 3H), and  $m/z$  EIMS 500.

**General procedure of polymerization.** Under inert conditions (Ar), dibromo-monomer (0.5 mmol) and compound (**1**) (0.5 mmol) were dissolved in toluene (20 mL). Then,  $\text{Pd}_2(\text{dba})_3$

(2 mol% ) and P(o-Tolyl)<sub>3</sub> (16%) were added into the mixture. The mixture was heated to 110°C and stirred for 24 hr under Ar condition. 2-tributylstannyl thiophene (39.5 μL) was added to the mixture and then after two hours, 2-bromothiophene (12.5 μL) was added. The mixture was further stirred overnight to complete the end-capping reaction. The mixture was cooled to room temperature and poured slowly in methanol. The solid was collected through 0.45 μm nylon filter and washed with methanol and acetone in a soxhlet apparatus to remove the oligomers and catalyst residue. Finally the mixture was extracted with chloroform and the final polymer was collected via reprecipitation into methanol.

*PBTCT*. Mn (13,300), Mw (28,000), and PDI (2.1)

*PBTCTO*. Mn (10,500), Mw (24,200), and PDI (2.3)

*PBTPDO*. Mn (11,500), Mw (25,300), and PDI (2.2)

*PBTFD0*. Mn (11,600), Mw (22,000), and PDI (1.9)

*PBT8PT*. Mn (23,000), Mw (60,000), and PDI (2.6)

## REFERENCES

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