Supporting Information

Solution Phase Exciton Diffusion Dynamics of a Charge-transfer Copolymer **PTB7** and a Homopolymer **P3HT**

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Chart S1. TD-DFT calculation outputs of **PTB7** oligomer with 5 **TT-BDT** units and **P3HT** oligomer with 9 thiophenes.

PTB7 oligomer

Excited State 1: Singlet-A 1.8855 eV 657.57 nm f=4.2941 <S**2>=0.000
H−1 → L+1 6.9% (-0.18551)
HOMO → LUMO 90.4% (0.67244)

Excited State 2: Singlet-A 2.1301 eV 582.06 nm f=0.0080 <S**2>=0.000
H −2 → L+1 2.3% (0.10735)
H −1 → LUMO 81.9% (0.64008)
HOMO → L+1 14.6% (-0.27048)

Excited State 3: Singlet-A 2.1818 eV 568.26 nm f=0.0109 <S**2>=0.000
H −1 → LUMO 13.4% (0.26027)
H −1 → L+2 3.1% (0.12350)
HOMO → L+1 80.9% (0.63583)

P3HT oligomer

Excited State 1: Singlet-A 2.0335 eV 609.72 nm f=3.0114 <S**2>=0.000
HOMO → LUMO 98.0% (0.69987)

Excited State 2: Singlet-A 2.4133 eV 513.76 nm f=0.1688 <S**2>=0.000
H −1 → LUMO 45.5% (-0.47704)
HOMO → L+1 51.4% (0.50700)

Excited State 3: Singlet-A 2.6061 eV 475.75 nm f=0.0011 <S**2>=0.000
H −1 → LUMO 52.0% (0.50974)
HOMO → L+1 46.5% (0.48229)

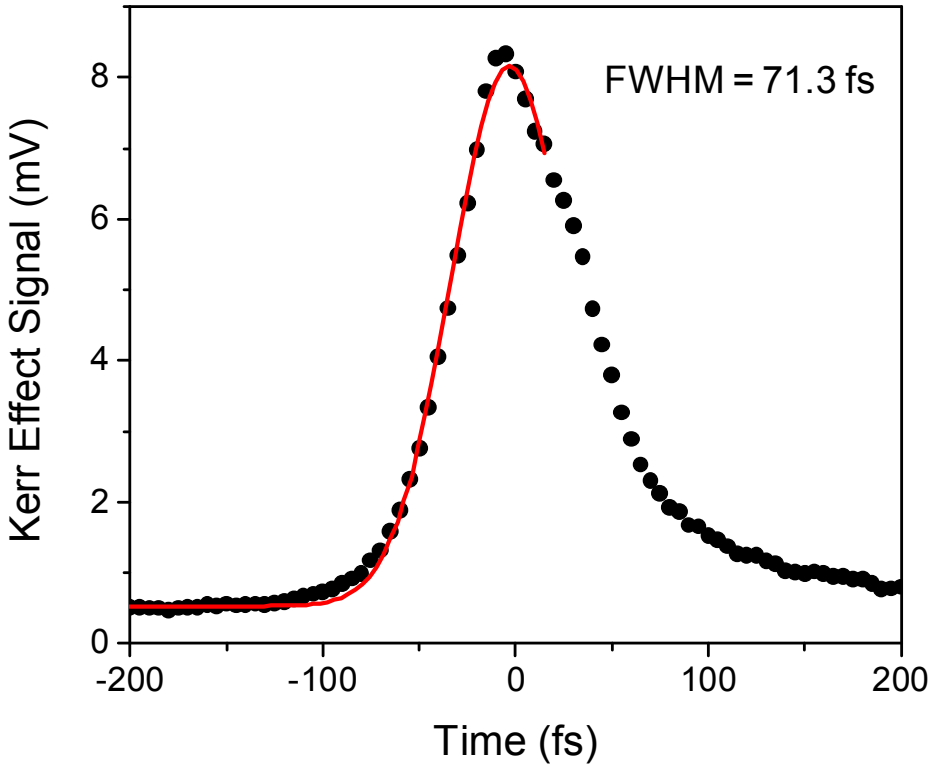

Figure S1. Instrumental response function (IRF) by using an optical Kerr effect signal of MeOH at 510 nm. The asymmetry in the tail is caused by the solvent nuclear dynamics.[a]

[a] N. A. Smith, S. Lin, S. R. Meech, K. Yoshihara *J. Phys. Chem. A* **1997,** *101,* 3641.

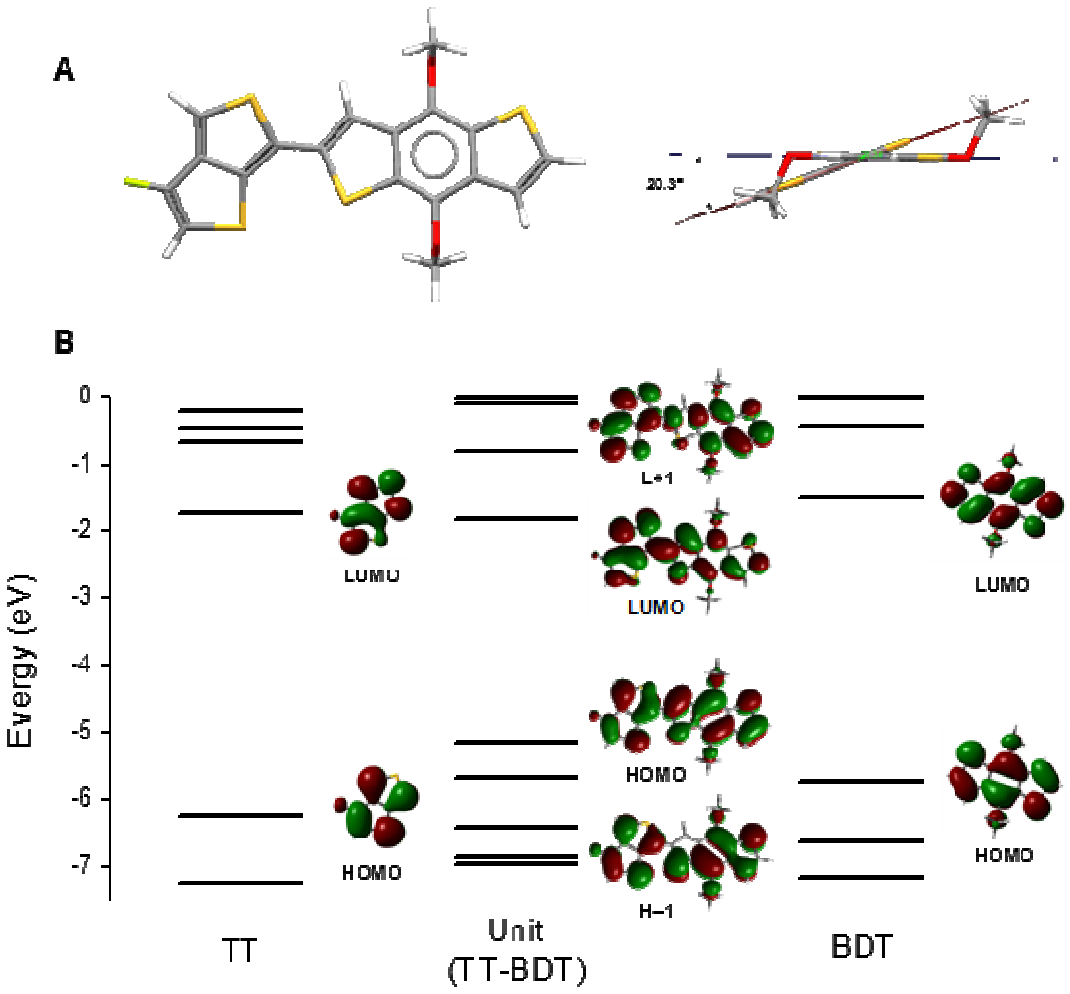

Figure S2. (A) Optimized molecular structure of **TT-BDT** and (B) frontier MO diagrams of **TT**, **BDT**, and **TT-BDT**(isosurface value: 0.02).

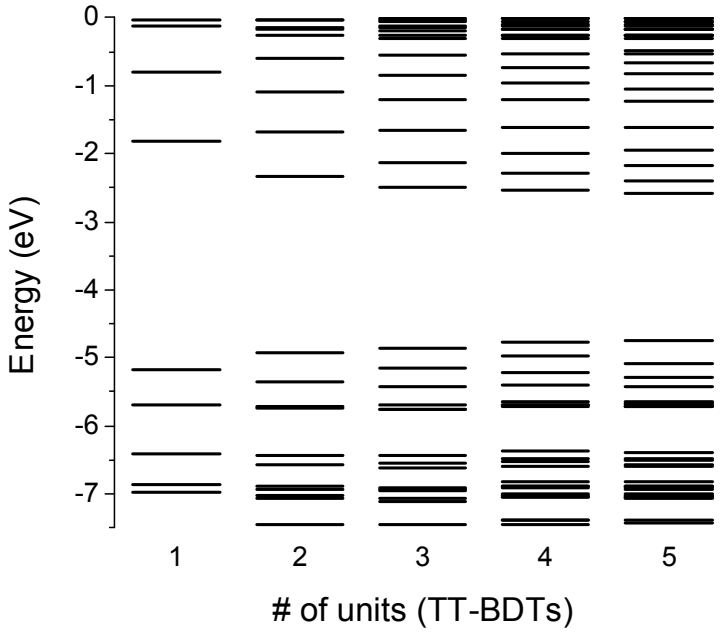

Figure S3. Energetic MO diagram of **PTB7** oligomers.

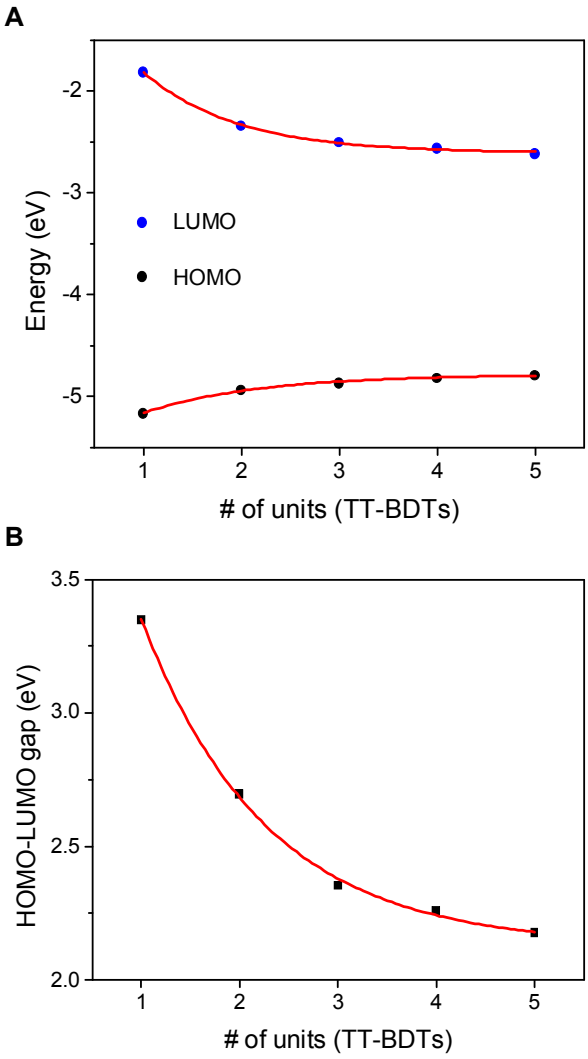

Figure S4. (A) Energy levels of the HOMO and LUMO and (B) the HOMO-LUMO gap of **PTB7** oligomers.

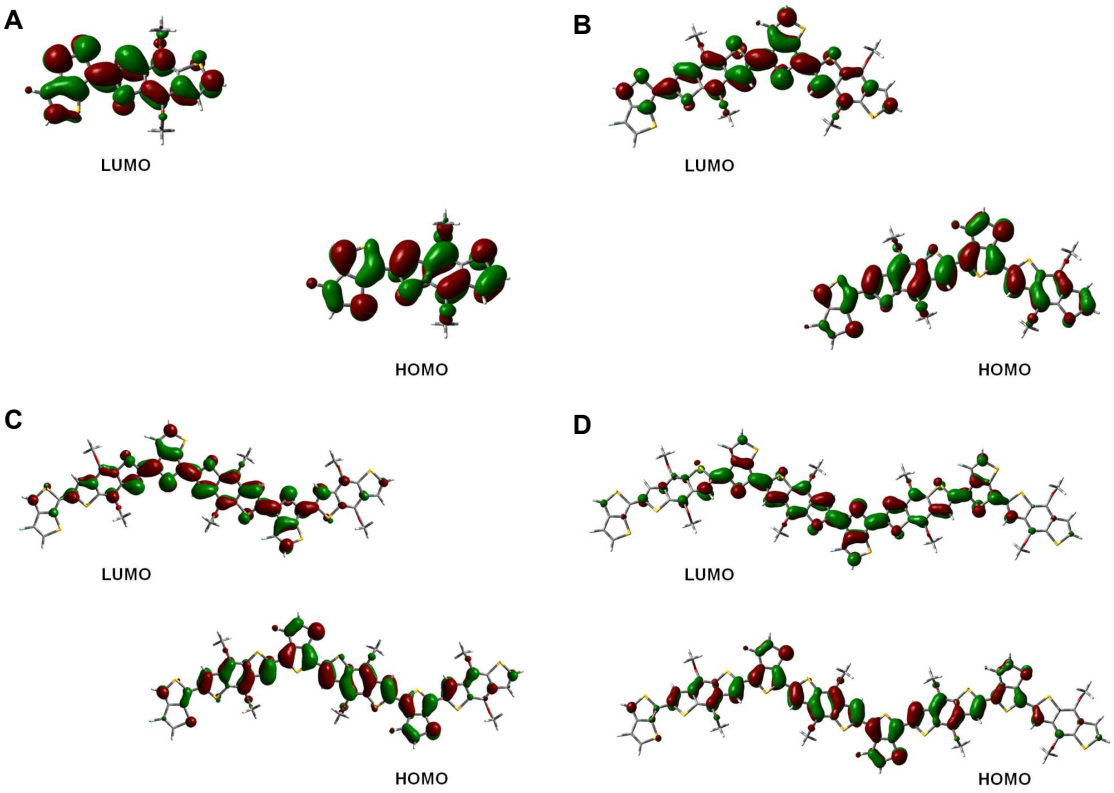

Figure S5. Frontier MO diagrams of **PTB7** oligomers with (A) one, (B) two, (D) three, and four **TT-BDT** units (isosurface value: 0.02).

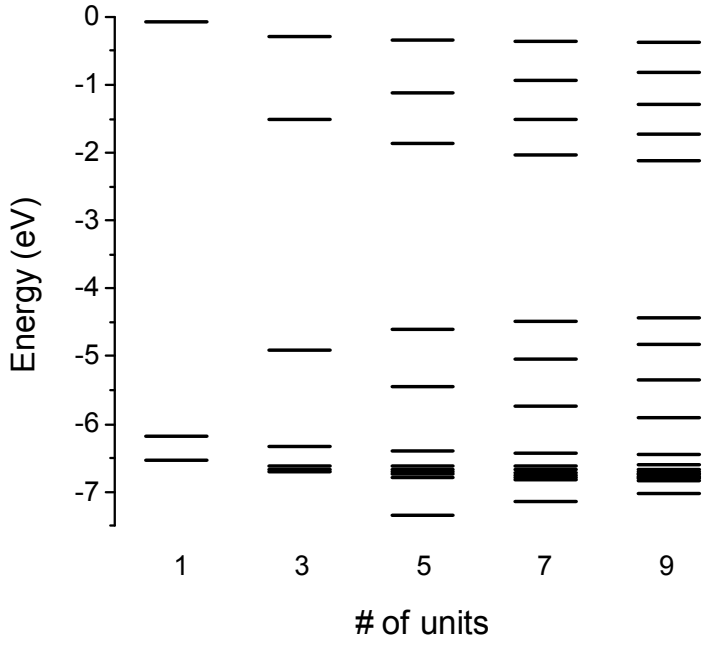

Figure S6. Energetic MO diagram of **P3HT** oligomers.

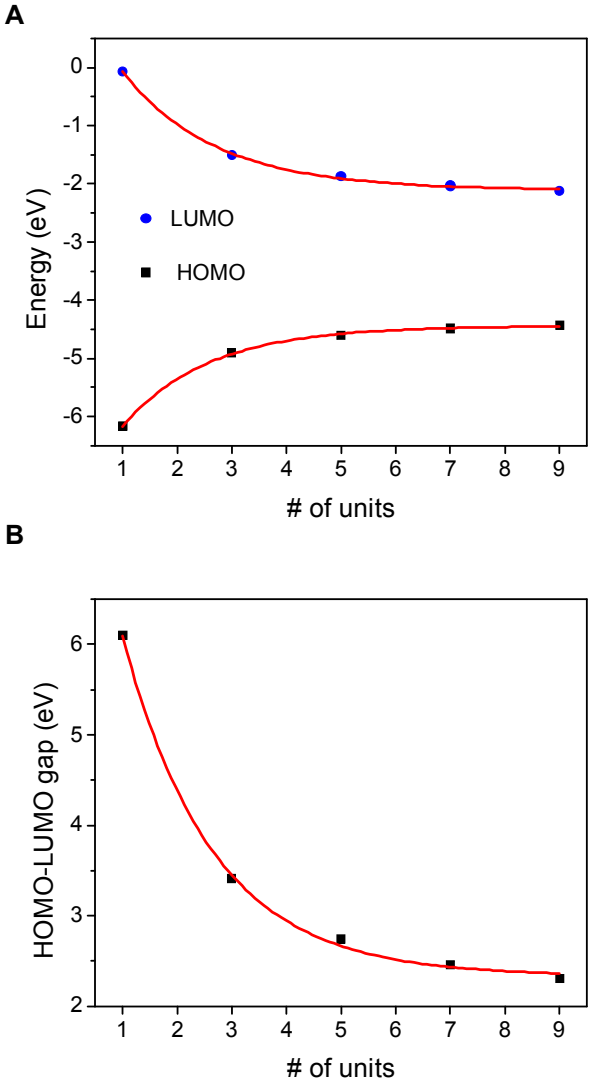

Figure S7. (A) Energy levels of the HOMO and LUMO and (B) the HOMO-LUMO gap of **P3HT** oligomers.

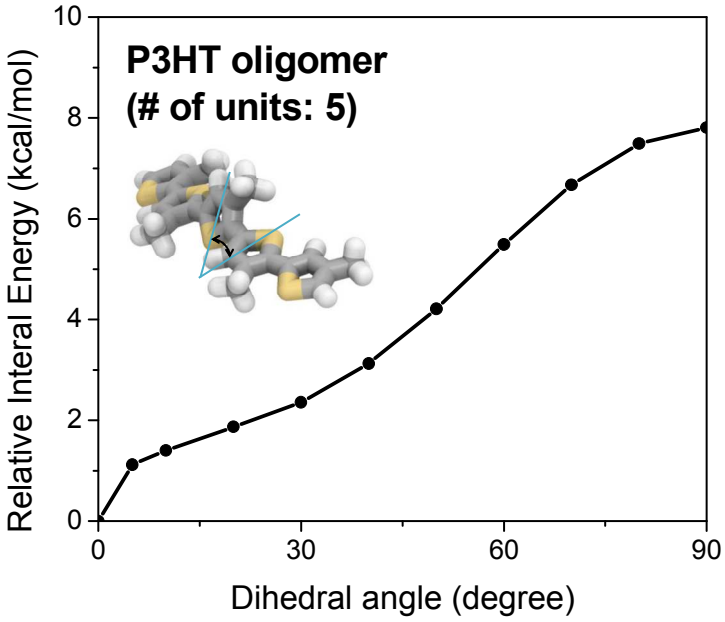

Figure S8. Relative internal energies of **P3HT** oligomer with five thiophenes, depending on various dihedral angles between the central thiophene and its neighboring coplanar thiophens.