Supporting Information

Evidence of Molecular Structure Dependent Charge Transfer Between Isoindigo-Based Polymers and Fullerene

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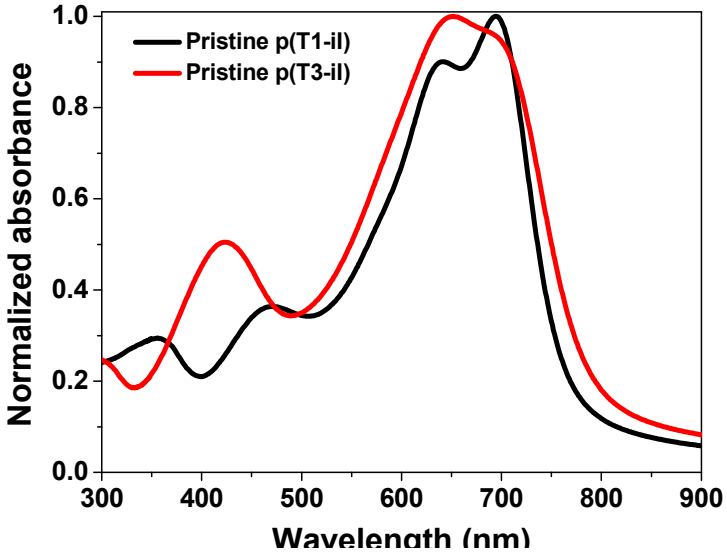

Figure S1. Normalized absorption spectra for P(T1-iI) and P(T3-iI) polymers.

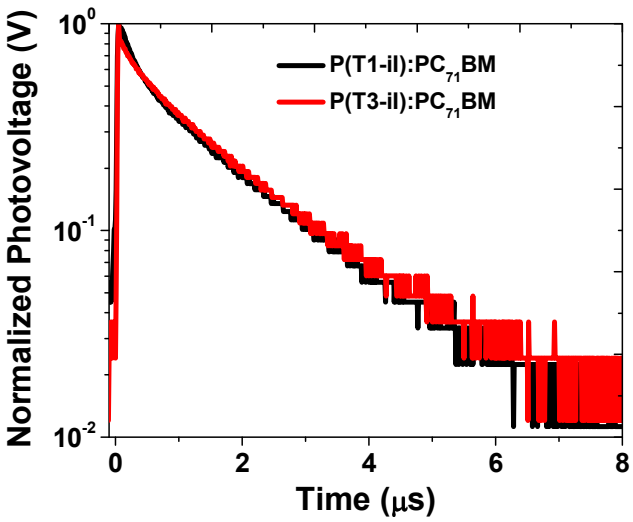

Figure S2. Transient photovoltage (TPV) decay measured for P(T1-iI):PC71BM and P(T3-iI):PC71BM devices. The data show a carrier lifetime of 1.38 μs and 1.25μs respectively. This indicates nearly identical bimolecular recombination rates.

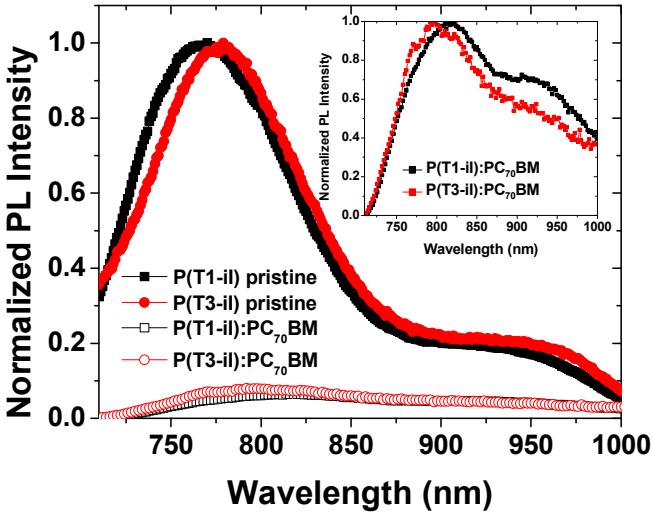

Figure S3. Normalized steady-state photoluminescence spectra for pristine P(T1-iI) and P(T3-iI) films along with the PL spectra for the P(T1-iI):PC_{70}BM and P(T3-iI):PC_{70}BM blends relative to the corresponding pristine polymers. PL is almost completely quenched after blending with PC_{70}BM in both cases. Inset: Normalized PL spectra for P(T1-iI):PC_{70}BM and P(T3-iI):PC_{70}BM blends.

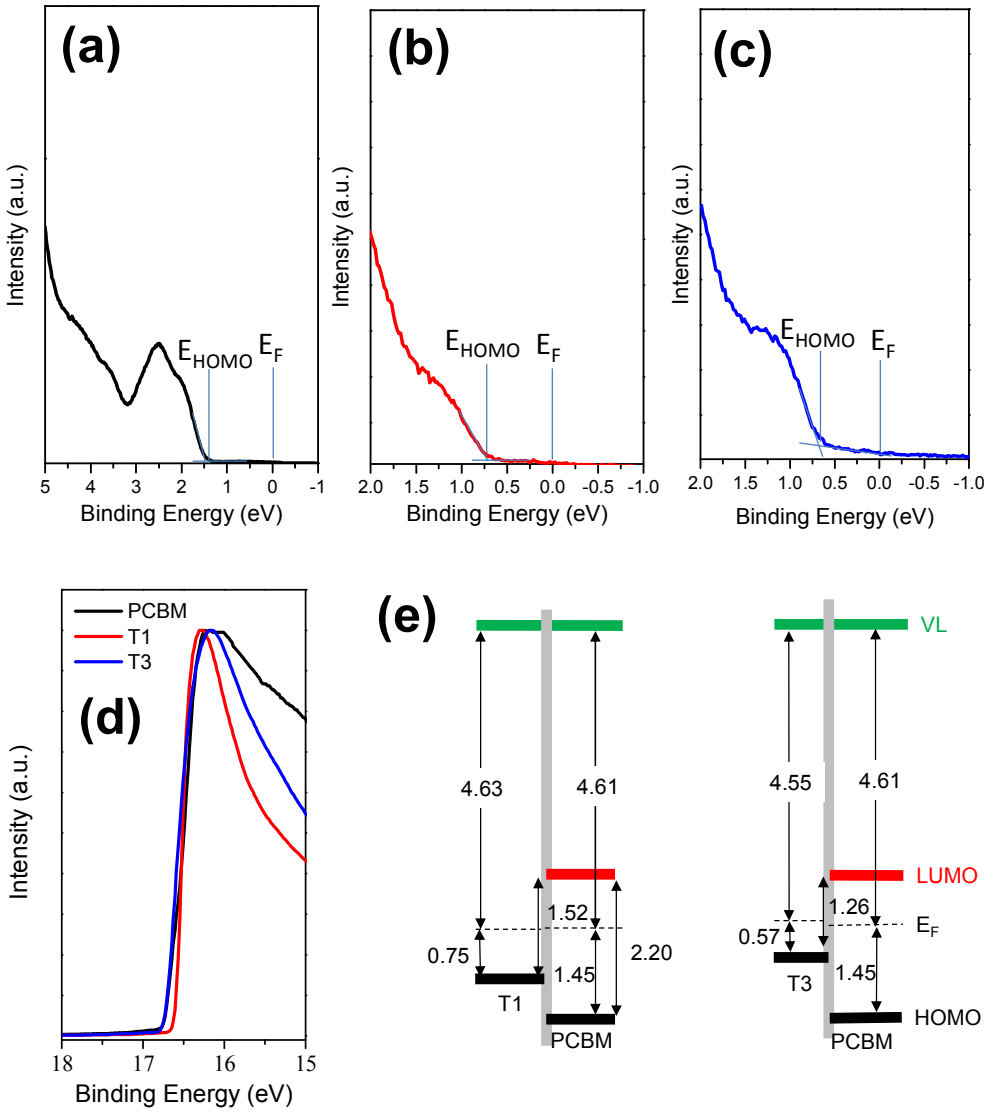

Figure S4. Photoemission spectroscopy spectra of HOMO energies of (a) $PC_{71}BM$ = 1.45 eV, (b) P(T1-iI) = 0.75 eV, and (c) P(T3-iI) = 0.57 eV relative to the Fermi level, E_F. (d) Secondary electron cutoff spectra for $PC_{71}BM$, T1 and T3, and the extracted work-functions are 4.61 eV, 4.63 eV, and 4.55 eV respectively. (e) Assuming vacuum level alignment, without interface dipole, and taking the transporting gap of $PC_{71}BM$ with 2.20 eV, we obtained the effective bandgap E_{eff} of 1.58 eV for P(T1-iI):$PC_{71}BM$ and 1.39 eV for P(T3-iI):$PC_{71}BM$.

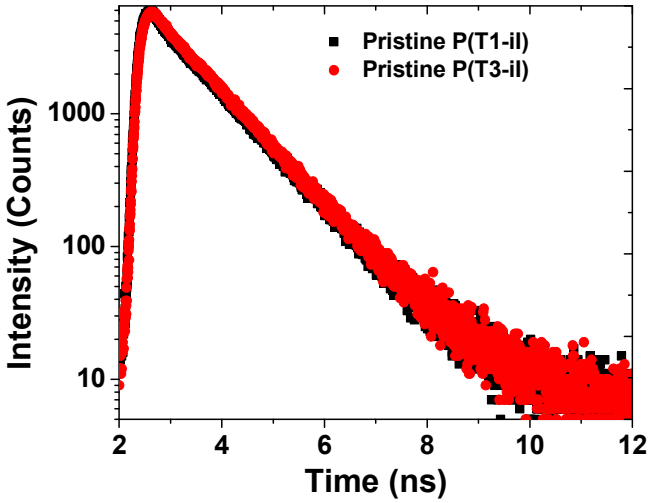

Figure S5. Transient PL for pristine P(T1-iI) and P(T3-iI) shows single exponential decays.

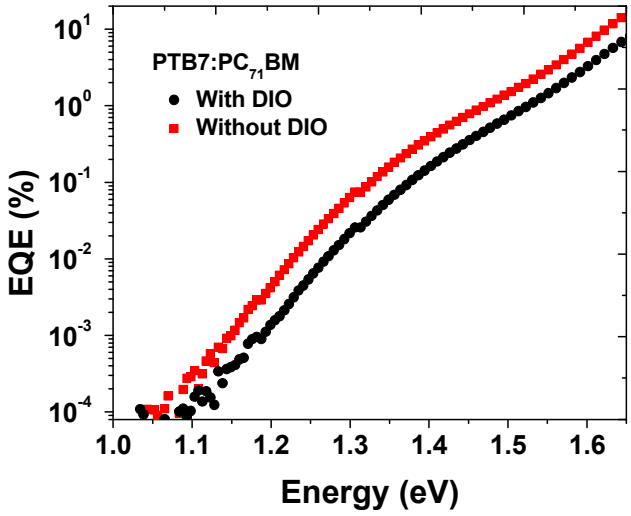

Figure S6. Sub-bandgap EQE of PTB7:$PC_{71}BM$ with or without DIO as solvent additive. No significant difference in CT cutoff is observed despite the difference in morphology.

Dielectric constant of materials used in this study:

The dielectric constants PTB7:$PC_{71}BM$ blends were measured with or without additive 1,8-Diiodooctane (DIO). The blend with DIO showed a dielectric constant of 5.03 ± 0.22 and the one without DIO have a dielectric constant of 4.87 ± 0.15. No significant difference is observed.

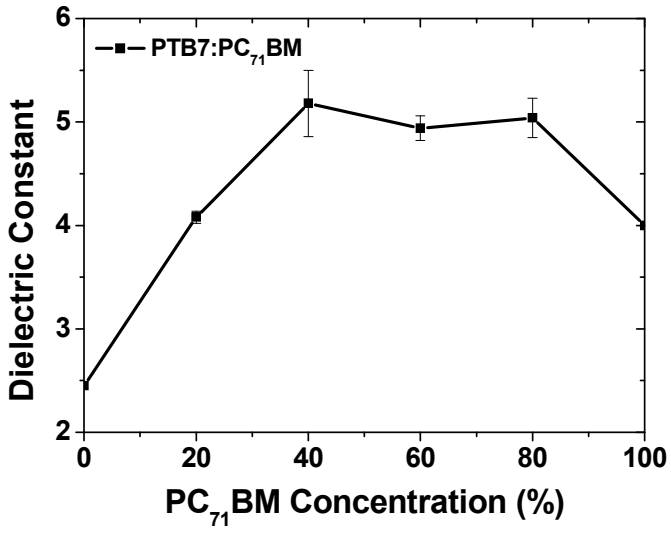

Figure S7. Dielectric constants of P(T3-iI):$PC_{71}BM$ blend film with different weight percentage of $PC_{71}BM$.

Density Functional Theory (DFT) Electronic Structure Calculations:

Gaussian 09 was used to perform all calculations. The alkyl groups on terthiophene and isoindigo were replaced for methyl to reduce the computational cost. The T1-iI monomer, dimer, trimer and tetramer, and T3-iI monomer, dimer, and trimer were built and optimized sequentially. The unconstrained geometries of the oligomers in gas phase were optimized by DFT using the B3LYP hybrid functional and the 6-31G (d) basis set. Frequency calculations were performed to characterize the stationary points obtained after self-consistent field convergence using the same functional/basis set method, and all minima reported here possessed no imaginary frequencies.

All Kohn-Sham orbital maps are presented as computed at the B3LYP/6-31G(d) level, and plotted using an isodensity value of 0.04 e/bohr^3 unless otherwise noted. Kohn-Sham orbital maps are reported for T1-il model trimer and T3-iI model dimer as they exhibit a comparable number of double bonds for the two structures.

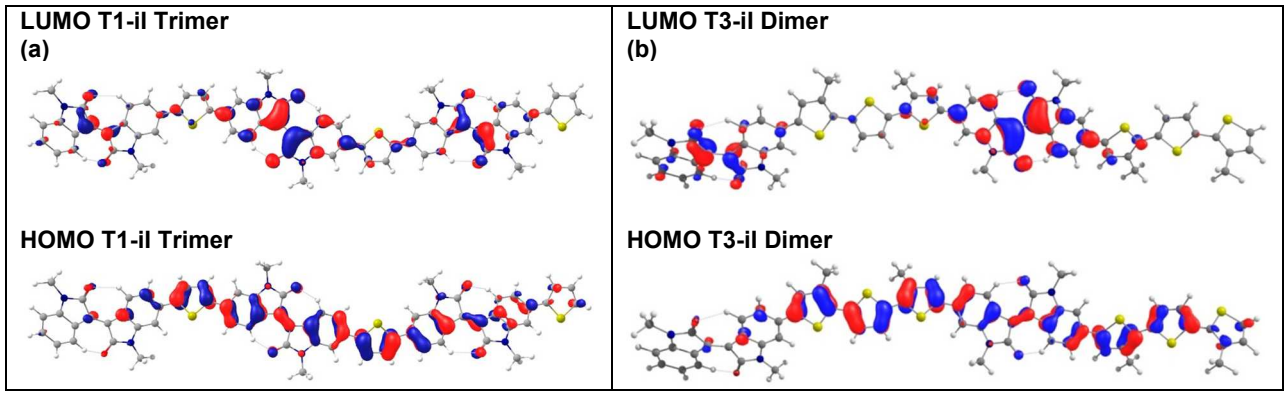

Figure S8. (a) Isodensity surfaces (0.04 e/bohr^3) of the frontier orbitals and energies of a T-iI trimer. (b) Isodensity surfaces (0.04 e/bohr^3) of the frontier orbitals and energies of a T3-iI dimer.