A Comparative Theoretical Study of Exciton-Dissociation and Charge-Recombination Processes in Oligothiophene/Fullerene and Oligothiophene/Perylenediimide Complexes for Organic Solar Cells

Yuanping Yi, Veaceslav Coropceanu, and Jean-Luc Brédas*

School of Chemistry and Biochemistry

and

Center for Organic Photonics and Electronics

Georgia Institute of Technology

Atlanta, Georgia 30332-0400

SUPPLEMENTARY INFORMATION:

Calculated electron-transfer rates for configurations a, b, and c using EA values of -3.95, -3.7, and -3.5 eV; calculated Coulomb energies, electronic couplings, and electron-transfer rates for intermolecular orientations generated by rotating the PDI and 6T molecules along the long molecular axis and the central carbon-carbon single bond, respectively.
(a) $k_{50} \ (s^{-1})$  
(b) $k_{51A} \ (s^{-1})$  
(c) $k_{51D} \ (s^{-1})$  

$EA = -3.95 \ eV$
(a) $k_{S0} (s^{-1})$  $k_{S1A} (s^{-1})$  $k_{S1D} (s^{-1})$  $EA = -3.7$ eV

(b) $k_{S0} (s^{-1})$  $k_{S1A} (s^{-1})$  $k_{S1D} (s^{-1})$

(c) $k_{S0} (s^{-1})$  $k_{S1A} (s^{-1})$  $k_{S1D} (s^{-1})$
Figure S1. Evolution of the CR rate from the lowest CT state to the ground state ($k_{S0}$) and of the CT rates from the lowest singlet state on PDI or C_{60} ($k_{S1A}$) and on 6T ($k_{S1D}$) to the lowest CT state, as a function of the displacements of 6T along the long and short axes, for complexes 6T/PDI (configuration a) and 6T/C_{60} (configurations b and c). From top to bottom, EA = -3.95, -3.7, and -3.5 eV, respectively.
Figure S2. Calculated Coulomb energy of the lowest CT state as a function of the rotation angles along the long axis of PDI and the central carbon-carbon single bond of 6T for complexes 6T/PDI and 6T/C₆₀, respectively.
Figure S3. Electronic couplings to the lowest CT state for the ground state ($V_{S0}$) and for the lowest local-excited singlet state on PDI or C$_{60}$ ($V_{S1A}$) and on 6T ($V_{S1D}$), as a function of the rotation angles along the long axis of PDI and the central carbon-carbon single bond of 6T, for complexes 6T/PDI and 6T/C$_{60}$, respectively.
\( \phi_d = 3.5 + 2.5 \sin \phi \)

\( \phi_d = 3.5 + 1.5 \cos \phi \)

\[ \text{EA} = -3.95 \text{ eV} \]

\[ \text{EA} = -3.8 \text{ eV} \]
Figure S4. The CR rate from the lowest CT state to the ground state ($k_{S0}$) and of the CT rates from the lowest local-excited singlet state on PDI or C$_{60}$ ($k_{S1A}$) and on 6T ($k_{S1D}$) to the lowest CT state, as a function of the rotation angles along the long axis of PDI and the middle carbon-carbon single bond of 6T, for complexes 6T/PDI and 6T/C$_{60}$, respectively. From top to bottom, EA = -3.95, -3.8, -3.7, and -3.5 eV, respectively.