## Supporting Information

# Local Excitation/Charge Transfer Hybridization Simultaneously Promotes Charge Generation and Reduces Non-Radiative Voltage Loss in Non-Fullerene Organic Solar Cells 

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(a)

(b)

(c)


Figure Si. Chemical structures of (a) DRTB-T and (b) IT-4F and (c) their frontier molecular orbitals energy levels. Note that, the experimental LUMO energy levels were calculated by the HOMO energy plus optical bandgap (including incorrectly the exciton binding energy).


Figure S2. Side views of DFT- $\omega \mathrm{B} 97 \mathrm{XD} / 6-31 \mathrm{G}^{* *}$ optimized geometries of 2 (DRTB-T), $2(\mathrm{IT}-4 \mathrm{~F})$, (DRTB-T)-(IT-4F), 2(DRTB-T)-(IT-4F), and (DRTB-T)-2(IT-4F).
(a) 2(DRTB-T)-(IT-4F)

(b) (DRTB-T)-2(IT-4F)


Figure $\mathbf{S}_{3}$. Electron-hole density maps (red: electron; blue: hole) for the higher-level LE states: (a) 2(DRTB-T)-(IT-4F) and (b) (DRTB-T)-2(IT-4F). Note that, S4A and S5A has a hybridized LE/CT character in the IT-4F molecules.


Figure S4. (a) Excitation energies calculated by TDDFT at the PCM-tuned- $\omega$ B97XD/6-31G** level for (DRTB-T)-( $\mathrm{PC}_{71} \mathrm{BM}$ ) and (b) electron-hole density maps (red: electron; blue: hole) for relevant excited states. The DFT- $\omega$ B97XD/6-31G** optimized geometry of (DRTB-T)-( $\mathrm{PC}_{71} \mathrm{BM}$ ) is an inset of (a).

Table Sı. Excitation energies (eV), oscillator strengths ( $f$ ), main electronic transitions (weights $\geq$ $5 \%$ ) of the first singlet excited state ( $\mathrm{S}_{1}$ ) and frontier molecular orbitals along with energy levels (eV) of DRTB-T, 2 (DRTB-T), IT-4F, and 2 (IT-4F).

|  | DRTB-T | 2(DRTB-T) | IT-4F | 2(IT-4F) |
| :---: | :---: | :---: | :---: | :---: |
| S1 (f) | 2.093 (3.206) | 2.071 (5.772) | 1.790 (2.886) | 1.715 (5.036) |
|  | HOMO -> LUMO (92\%) HOMO-1 -> LUMO+1 (6\%) | $\begin{aligned} & \text { HOMO -> LUMO } \\ & (63 \%) \\ & \text { HOMO-1 -> } \\ & \text { LUMO+1 (28\%) } \end{aligned}$ | $\begin{aligned} & \text { HOMO } \\ & \text { LUMO (97\%) }^{->} \end{aligned}$ | $\begin{aligned} & \text { HOMO -> LUMO } \\ & \text { (81\%) } \\ & \text { HOMO-1 } \\ & \text { LUMO+1 (17\%) } \end{aligned}$ |
| LUMO+1 | -20000 \% O $-2.544$ |  |  |  |
| LUMO |  |  |  $-3.201$ |  |
| HOMO |  $-5.227$ |  -5.186 |  |  |
| HOMO-1 |  |  $-5.187$ | $\begin{gathered} -30^{\circ}+900^{\circ \circ} \\ -6.155 \end{gathered}$ |  |

Table S2. Excitation energies (eV), oscillator strengths ( $f$ ), main electronic transitions (weights $\geq$ $5 \%$ ) of the low-lying singlet excited states and frontier molecular orbitals along with energy levels (eV) of (DRTB-T)-(IT-4F), 2(DRTB-T)-(IT-4F), and (DRTB-T)-2(IT-4F) (red: D -> A transitions).

|  | (DRTB-T)-(IT-4F) | 2(DRTB-T)-(IT-4F) | (DRTB-T)-2(IT-4F) |
| :---: | :---: | :---: | :---: |
| S1 (f) | CTi: 1.706 (0.876) | CTi:1.705 (0.845) | S1A/CT1: 1.685 (2.761) |
|  | HOMO (D) -> <br> LUMO (A) (66\%)  <br> HOMO-1 (A) (A <br> LUMO (A) (17\%)  <br> HOMO (D)  <br> LUMO+1 (A) (10\%)  | HOMO (D) -> LUMO <br> (A) (66\%) <br> HOMO-2 (A) -> LUMO <br> (A) (17\%) <br> HOMO (D) -> LUMO+1 <br> (A) (10\%) | HOMO (D) |
|  |  |  | LUMO (A) (30\%) |
|  |  |  | HOMO-1 (A) |
|  |  |  | LUMO (A) (29\%) |
|  |  |  | HOMO (D) |
|  |  |  | LUMO+1 (A) (18\%) |
|  |  |  | HOMO-1 (A) -> |
|  |  |  | LUMO+1 (A) (8\%) |
| S2 (f) | SıA: 1.800 (2.442) | SıA: 1.799 (2.510) | S2A/CT1: 1.734 (2.519) |
|  | HOMO-1 (A) -> | HOMO-2 (A) -> LUMO | HOMO-1 (A) |
|  | LUMO (A) (67\%) | (A) (63\%) | LUMO (A) (32\%) |
|  | HOMO-2 (D) -> | HOMO-3 (D-A) -> | HOMO-2 (A) -> |
|  | LUMO (A) (18\%) | LUMO (A) (18\%) | LUMO (A) (23\%) |


|  | $\begin{array}{lll} \hline \text { HOMO (D) } & \text {-> } \\ \text { LUMO (A) (8\%) } \end{array}$ | $\begin{aligned} & \text { HOMO (D) -> LUMO } \\ & \text { (A) (8\%) } \end{aligned}$ | HOMO (D) -> <br> LUMO (A) (16\%)  <br> HOMO (D) -> <br> LUMO+1 (A) (11\%)  <br> HOMO-3 (D-A) -> <br> LUMO+1 (A) (5\%)  |
| :---: | :---: | :---: | :---: |
| S3 (f) | CT2: 1.956 (o.019) | CS: 1.909 (0.000) | S3A: 1.792 (0.020) |
|  | HOMO (D) -> LUMO+1 (A) (31\%) HOMO (D) LUMO (A) (25\%) HOMO-2 (D) LUMO (A) (19\%) HOMO-2 (D) LUMO+1 (A) (7\%) HOMO-3 (D) LUMO (A) (5\%) | $\begin{aligned} & \text { HOMO-1 (D) -> LUMO } \\ & \text { (A) (100\%) } \end{aligned}$ |  |
| S4 (f) | CT3: 2.041 (0.227) | CT2: 1.951 (0.025) | CS: 1.817 (0.079) |
|  | $\left.\begin{array}{l} \text { HOMO (D) } \\ \text { LUMO+1 (A) (36\%) } \\ \text { HOMO-2 (D) } \\ \text { LUMO (A) } \\ \text { (31\%) } \end{array}\right)$ | HOMO (D) -> LUMO+1 <br> (A) (31\%) <br> HOMO (D) -> LUMO <br> (A) (24\%) <br> HOMO-3 (D-A) -> <br> LUMO (A) (13\%) <br> HOMO-5 (D) -> LUMO <br> (A) (6\%) <br> HOMO-2 (A) -> LUMO <br> (A) (6\%) |  |
| $\mathrm{S}_{5}(f)$ | SıD: 2.053 (2.190) | SiD/CT3: 2.036 (1.240) | S4A: 1.903 (0.437) |
|  | $\begin{array}{lll} \hline \text { HOMO } & \text { (D) } & -> \\ \text { LUMO+2 } & \text { (D) } & (74 \%) \\ \text { HOMO } & \text { (D) } & -> \\ \text { LUMO+1 } & \text { (A) } & (11 \%) \end{array}$ | $\begin{aligned} & \text { HOMO (D) -> LUMO+2 } \\ & \text { (D) (36\%) } \\ & \text { HOMO (D) -> LUMO+1 } \\ & \text { (A) (23\%) } \\ & \text { HOMO-3 (D-A) -> } \\ & \text { LUMO (A) (16\%) } \\ & \text { HOMO-5 (D) -> LUMO } \\ & \text { (A) (6\%) } \\ & \text { HOMO-4 (D) -> LUMO } \\ & \text { (A) (6\%) } \end{aligned}$ | HOMO-1 (A) -> <br> LUMO+1 (A) (46\%)  <br> HOMO-1 (A) -> <br> LUMO (A) (18\%)  <br> HOMO-1 (A) -> <br> LUMO+2 (A) (11\%)  <br> HOMO-2 (A) -> <br> LUMO (A) (6\%)  <br> HOMO-3 (D-A) -> <br> LUMO+1 (A) (6\%)  |
| S6 (f) |  | S1D/CT3': 2.044 (2.395) | S5A: 1.941 (0.604) |
|  |  | $\begin{aligned} & \text { HOMO (D) -> LUMO+2 } \\ & \text { (D) (45\%) } \\ & \text { HOMO (D) -> LUMO+1 } \\ & \text { (A) (25\%) } \\ & \text { HOMO-3 (D-A) -> } \\ & \text { LUMO (A) (7\%) } \\ & \hline \end{aligned}$ | HOMO-2 (A) -> LUMO+1 (A) (64\%) HOMO-2 (A) -> LUMO (A) (9\%) HOMO-3 (D-A) -> LUMO+1 (A) (7\%) |
| $\mathrm{S}_{7}(f)$ |  | S2D: 2.089 (1.814) | CT2: 1.953 (0.017) |


|  |  | HOMO-1 (D) -> <br> LUMO+3 (D) $(66 \%)$ <br> HOMO-1 (D)  <br> LUMO+2 (D) (21\%)  | HOMO (D) LUMO+1 (A) (35\%) HOMO (D) LUMO+2 (A) (16\%) HOMO (D) LUMO+3 (A) (12\%) -> |
| :---: | :---: | :---: | :---: |
| S8 (f) |  |  | CT3: 2.017 (0.000) |
|  |  |  | $\begin{aligned} & \text { HOMO-3 (D-A) } \\ & \text { LUMO (A) (36\%) } \\ & \text {-> } \\ & \text { HOMO (D) } \\ & \text { LUMO+2 (A) (31\%) } \\ & \text { HOMO (D) } \\ & \begin{array}{l} \text { LUMO+3 (A) (7\%) } \end{array} \\ & \begin{array}{lll} \text { HOMO-3 (D-A) } & \text {-> } \\ \text { LUMO+1 (A) (6\%) } \end{array} \\ & \begin{array}{ll} \text { HOMO-2 (A) } & \\ \text { LUMO (A) } & \text { (5\%) } \end{array} \\ & \hline \end{aligned}$ |
| S9 (f) |  |  | S1D: 2.050 (2.279) |
|  |  |  | $\begin{array}{\|lll\|} \hline \mathrm{HOMO} & \text { (D) } & -> \\ \text { LUMO+4 } & \text { (D) }(84 \%) \\ \hline \end{array}$ |
| LUMO+4 |  |  |  |
| LUMO+3 |  |  |  |
| LUMO+2 |  |  |  |
| LUMO+1 |  |  |  |
| LUMO |  |  |  |
| HOMO |  |  $5.175$ |  |


| HOMO-1 |  |  |  |
| :---: | :---: | :---: | :---: |
| HOMO-2 |  |  |  |
| HOMO-3 |  |  |  <br>  $-5.461$ |
| HOMO-4 |  |  $-5.461$ |  |
| HOMO-5 |  |  |  |

