Supplementary Information: Interfacial Photoinduced Carrier Dynamics Tuned by Polymerization of Coronene Molecules Encapsulated in Carbon Nanotubes: Bridging Type-I and -II Heterojunctions

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Nonadiabatic Dynamics Methods

Nonadiabatic carrier transfer dynamics simulations are carried out using Tully's fewest-switches surface-hopping methods based on density functional theory. [1-4] Time-dependent density functional theory in Kohn-Sham framework maps an interacting many-body system onto a system of noninteracting particles in which their electron densities equals to each other. As a result, time-dependent charge density $\rho(r,t)$ of an interacting system is obtained from a set of time-dependent Kohn–Sham orbitals $\psi_p(r,t)$ [5-9]

$$\rho(r,t) = \sum_{p=1}^{N_e} \left|\psi_p(r,t)\right|^2$$

Electron density evolution finally leads to a set of single-electron equations for evolution of Kohn–Sham orbitals $\psi_p(r,t)$ [10-14]

$$i\hbar \frac{\partial \psi_p(r,t)}{\partial t} = \hat{H}(r;R)\psi_p(r,t) \quad p = 1,2,\dots,N_e$$

If expanding time-dependent electron or hole wavefunction $\psi_p(r,t)$ in terms of interested unoccupied or occupied adiabatic Kohn–Sham orbitals $\phi_k(r,t)$ calculated from density functional theory calculations along adiabatic molecular dynamics trajectories

$$\psi_p(r,t) = \sum_k c_k(t)\phi_k(r;R)$$

one can obtain a set of equations of motion for expanding coefficients $c_j(t)$

$$i\hbar \frac{\partial c_j(t)}{\partial t} = \sum_k c_k(t)\left(\varepsilon_k \delta_{jk} - i\hbar d_{jk}\right)$$

where ε_k is energy of kth adiabatic state and d_{jk} is nonadiabatic coupling between adiabatic states j and k. The former is directly obtained from density functional theory calculations and the latter is calculated numerically through finite difference methods as overlaps of adiabatic states at times t and $t + \Delta t$:

$$d_{jk} = \left\langle \phi_j(r;R) \middle| \frac{\partial \phi_k(r;R)}{\partial t} \right\rangle \approx \frac{\langle \phi_j(t) | \phi_k(t+\Delta t) \rangle - \langle \phi_j(t+\Delta t) | \phi_k(t) \rangle}{2\Delta t}$$

in which $\phi_j(t)$ and $\phi_k(t+\Delta t)$ are wave functions of adiabatic states j and k at times t and $t+\Delta t$, respectively. Previous algorithms are primarily implemented with plane wave basis sets; [15-16] instead, we have recently implemented this nonadiabatic electron or hole dynamics method with Gaussian basis sets with CP2K [17-18] and have successfully applied to studying many materials. [19-22]

Carrier Transfer Analysis

To estimate electron or hole transfer from one to another fragment in nonadiabatic dynamics simulations, we have developed an efficient density-matrix based method. First, we can define a density matrix D in terms of atomic orbitals χ_μ

$$D_{\mu\nu i}(t) = p_i(t)\chi_{\mu i}\chi_{\nu i}^*$$

in which $p_i(t)$ is time-dependent occupation number of the ith adiabatic state calculated on the basis of above expanding coefficients $c_i(t)$; $\chi_{\mu i}$ is the μth atomic orbital coefficient of the ith adiabatic state. Similar to Mulliken charge analysis, [23] we have then defined a population matrix P using density matrix D and atomic overlap matrix S

$$P_{\mu\nu i} = D_{\mu\nu i}S_{\mu\nu}$$

Finally, we can obtain the ath atomic charge through summing all basis functions μ belonging to that atom and all involved adiabatic states i

$$P_a = \sum_i \left(\sum_{\mu\in a,\nu\in a} P_{\mu\nu i} + \frac{1}{2}\left(\sum_{\mu\in a,\nu\notin a} P_{\mu\nu i} + \sum_{\mu\notin a,\nu\in a} P_{\mu\nu i} \right) \right)$$

It should be noted that if only an atomic orbital belongs to the ath atom, just half of $P_{\mu\nu i}$ is used, as done by Mulliken charge analysis method. [21] Accordingly, total electron on a fragment A is done by summing all atomic charges belonging to that fragment

$$P_A = \sum_i p_i(t) P_{Ai}$$

in which

$$P_{Ai} = \sum_{a \in A} \left(\sum_{\mu \in a, \nu \in a} \chi_{\mu i} \chi_{\nu i}^* S_{\mu\nu} + \frac{1}{2} \left(\sum_{\mu \in a, \nu \notin a} \chi_{\mu i} \chi_{\nu i}^* S_{\mu\nu} + \sum_{\mu \notin a, \nu \in a} \chi_{\mu i} \chi_{\nu i}^* S_{\mu\nu} \right) \right)$$

In such a case, the differentiation of P_A is then derived as

$$\mathrm{d}P_A = d\left(\sum_i c_i^* c_i P_{Ai} \right) = \sum_i (d(c_i^* c_i) P_A + c_i^* c_i dP_{Ai})$$

in which the first term has variational occupations for adiabatic states i and the second term has constant adiabatic state occupations but changeable electron population. These two terms correspond to nonadiabatic and adiabatic electron transfer contributions. The former is mainly caused by state hoppings between different adiabatic states and the latter is primarily originated from changes of adiabatic states induced by atomic motions. Finally, it should be noted that Gaussian basis sets are used in our simulations, so molecular coefficients $\chi_{\mu i}$ are real numbers. Adiabatic states' expanding coefficients $c_i(t)$ are complex numbers, but they are not directly used; instead, their $c_i(t)c_i^*(t)$ products are used for calculating time-dependent occupation number $p_i(t)$ of the ith adiabatic state, which is a real number.
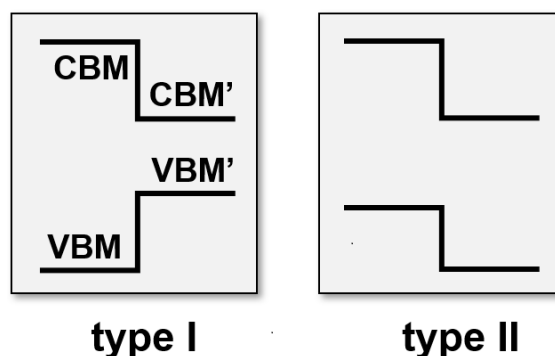
Additional Figures

Fig. S1 Schematic definition of the type-I and type-II heterojunctions widely used in the discipline of condensed matter.[24-26]

We have calculated time-dependent electron/hole populations for different numbers of trajectories in NAMD simulations. The results show that it is converged when more than 70*1000 trajectories (see Fig. S2). So our used 100*1000 trajectories are enough to get meaningful results.
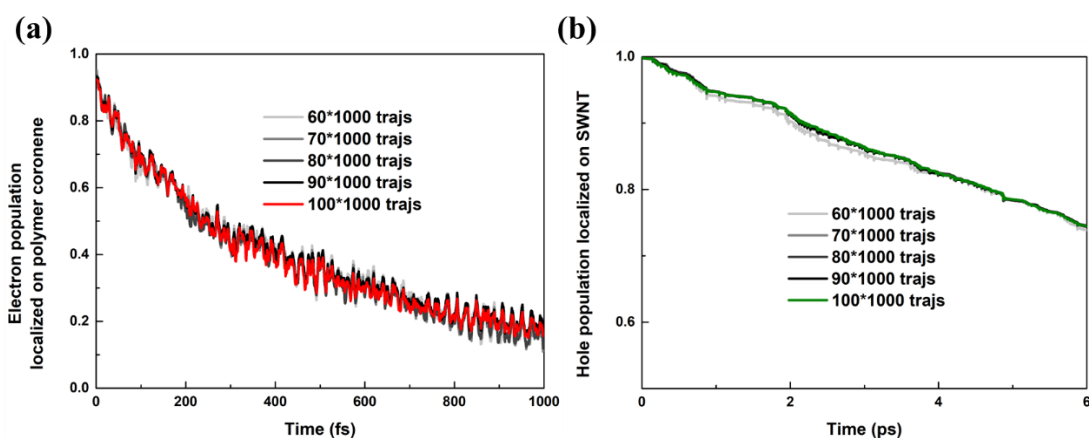

Fig. S2 Time-dependent electron amount remaining on the polymer coronene moiety (a), and hole amount on the SWNT moiety (b) calculated based on different numbers of trajectories in the nonadiabatic dynamics simulations.
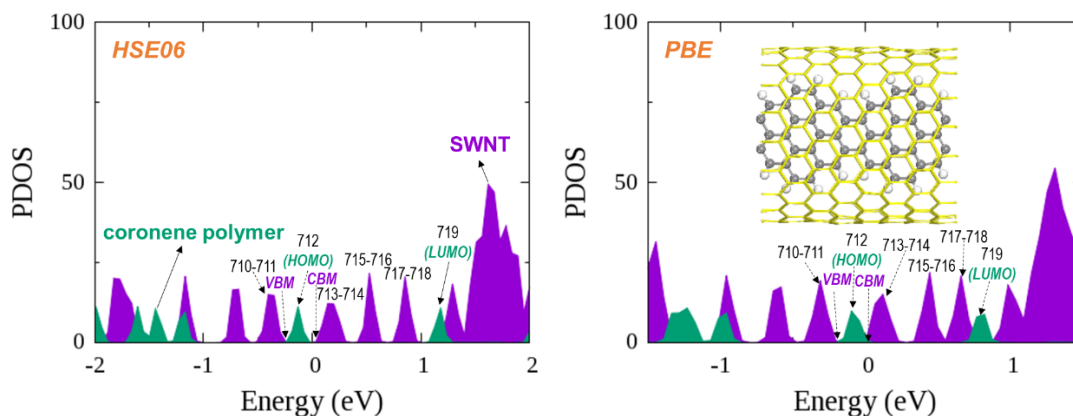
Fig. S3 The PDOS of corenene-polymer-encapsulated SWNT calculated at HSE06 level (left) and PBE+D3 level (right) when it's heated to 300 K. The schematic heterojunction structure shown is extracted from canonical molecular dynamics simulations at 300 K.
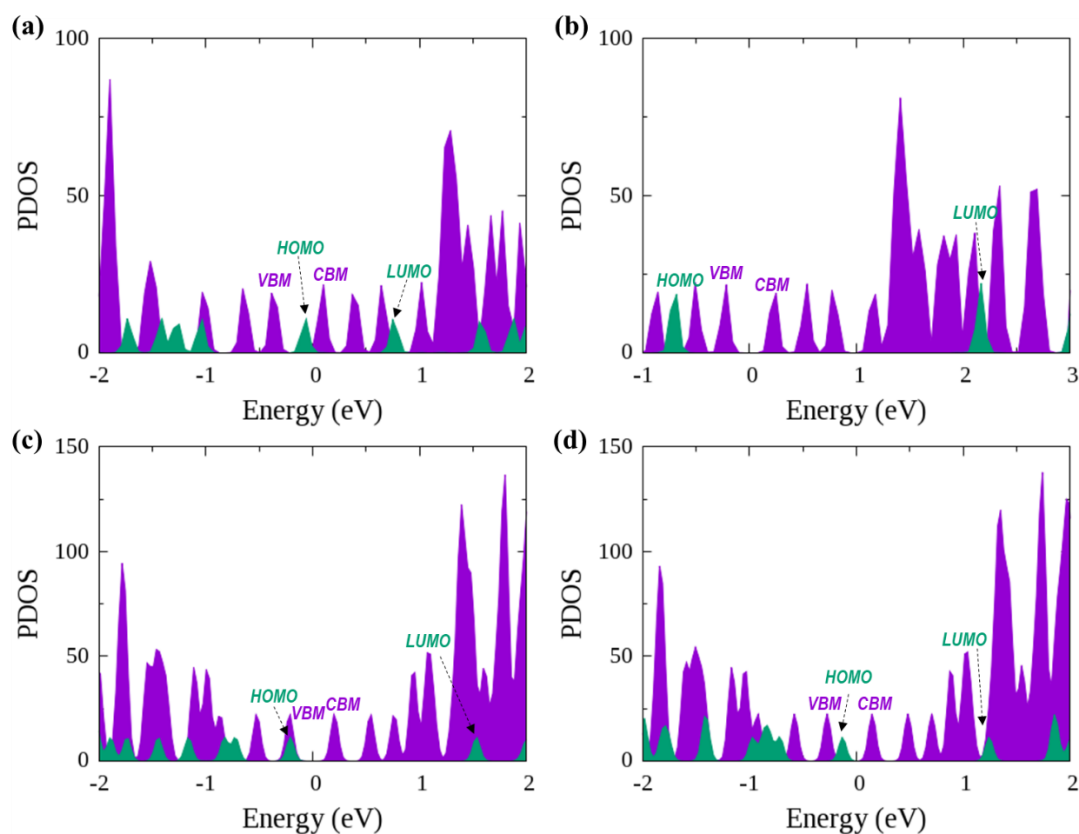

Fig. S4 PBE+D3 calculated projected density of states (PDOS) of (a) polymer@SWNT, (b) monomer@SWNT, (c) dimer@SWNT, and (d) trimer@SWNT.
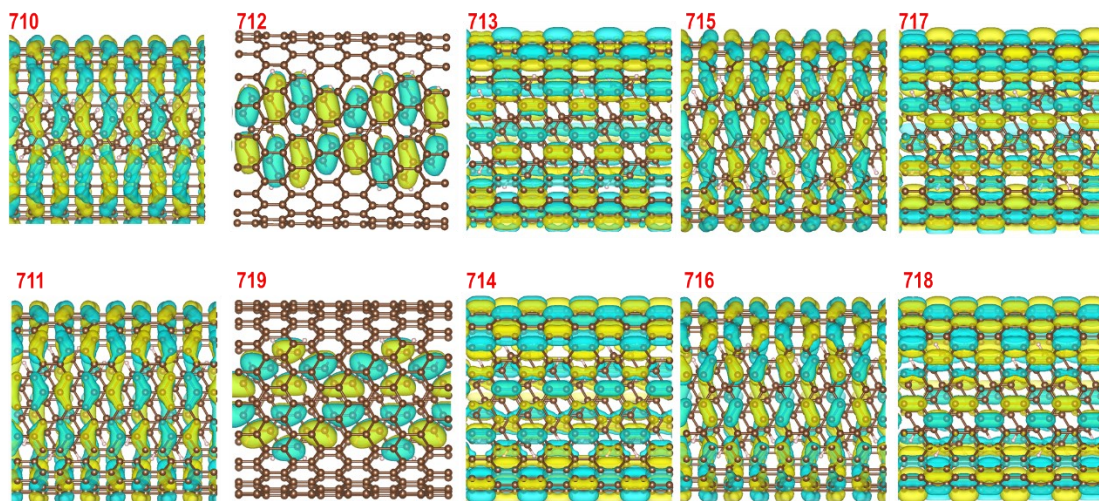
Fig. S5 Spatial distributions of ten adiabatic states involved in the interfacial electron and hole transfer dynamics of corenene-polymer-encapsulated SWNT calculated at PBE+D3 level.
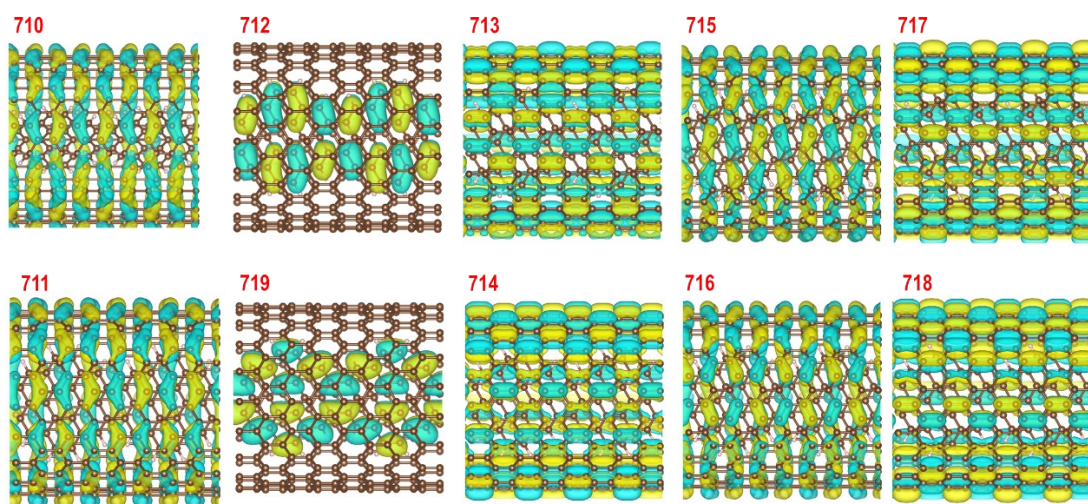

Fig. S6 Spatial distributions of ten adiabatic states involved in the interfacial electron and hole transfer dynamics of corenene-polymer-encapsulated SWNT calculated at HSE06 level.
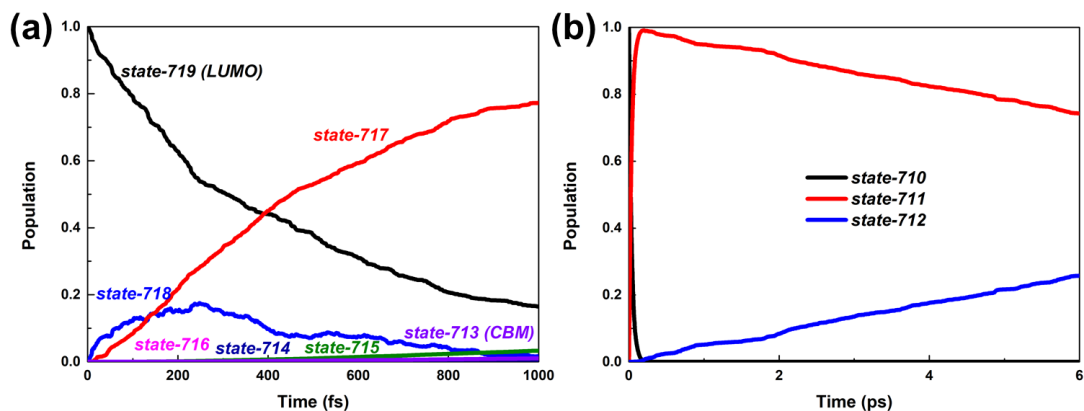
Fig. S7 Time-dependent state populations in electron transfer process (a) and hole transfer process (b).

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