

Electronic Supplementary Information:

**Photoinduced Electron Transfer from Carbon Nanotubes
to Fullerenes: C₆₀ versus C₇₀**

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Simulation Methods

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]

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

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 $c_j(t)$

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

where ε_k is energy of k th 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 $t + \Delta t$:

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

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 i th adiabatic state calculated on the basis of above expanding coefficients $c_i(t)$; $\chi_{\mu i}$ is the μ th atomic orbital coefficient of the i th 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 a th 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 a th 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

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

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 i th adiabatic state, which is a real number.

Additional Figures

PDOS Calculated at HSE06+D3 Level

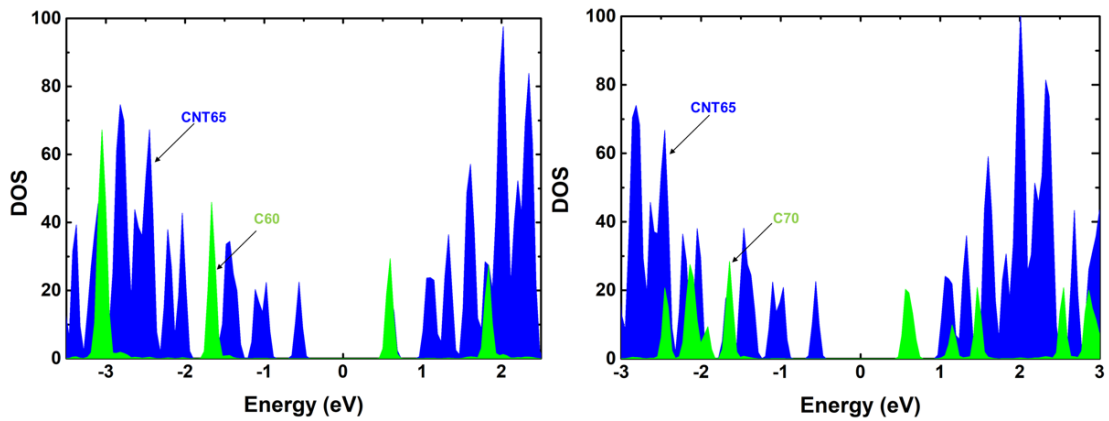


Figure S1: HSE06+D3 calculated projected density of states (PDOS) of C60@CNT65 (left) and C70@CNT65 (right).

Relevant Frontier States

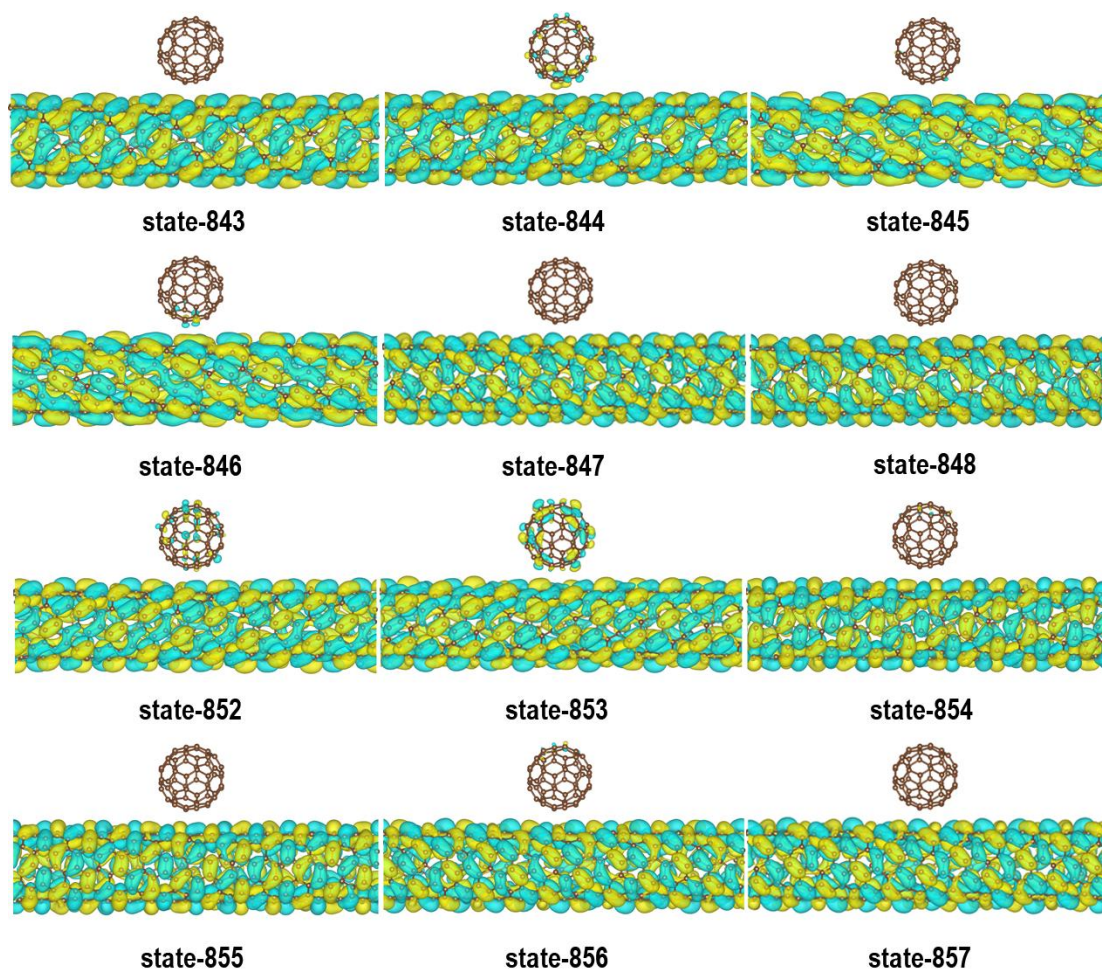


Figure S2: Frontier states of C60@CNT65 relevant to interfacial electron transfer dynamics.

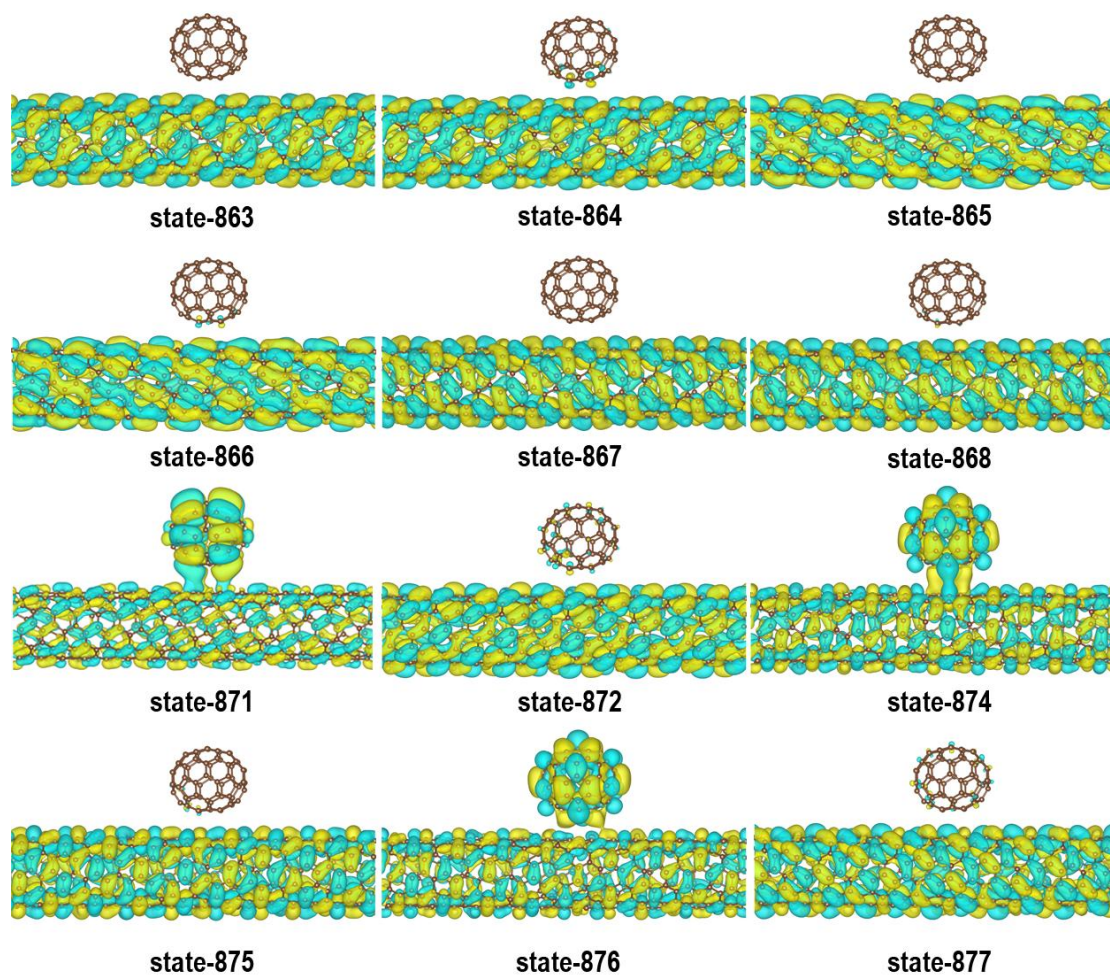


Figure S3: Frontier states of C70@CNT65 relevant to interfacial electron transfer dynamics.

Additional Tables

Table S1: Oscillator Strengths and Energies of All Excitations between Relevant Molecular Orbital Pairs in C60@CNT65 Calculated at PBE+D3 Level.

Transition (OK)	Osc.	Energy (eV)
848 → 852	0.75	0.93
847 → 852	1.93	0.93
848 → 853	1.91	0.93
847 → 853	0.75	0.93
844 → 856	0.56	1.83
844 → 857	0.71	1.84
843 → 856	0.71	1.84
843 → 857	0.57	1.84
840 → 860	0.64	2.27
839 → 861	0.85	2.28

Table S3: Oscillator Strengths and Energies of All Excitations between Relevant Molecular Orbital Pairs in C70@CNT65 Calculated at PBE+D3 Level.

Transition (OK)	Osc.	Energy (eV)
868 → 872	0.94	0.93
867 → 872	1.77	0.93
868 → 873	1.25	0.94
867 → 873	0.60	0.94
864 → 877	0.74	1.84
864 → 878	0.53	1.84
863 → 877	0.53	1.84
863 → 878	0.72	1.84
859 → 881	0.69	2.28
860 → 882	0.77	2.28

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