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Supporting Information: The Spin-Orbit Interaction Controls Photoinduced Interfacial Electron Transfer in Fullerene-Perovskite Heterojunctions: C_{60} versus C_{70}

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Methods

Nonadiabatic Carrier Dynamics Method

Nonadiabatic carrier transfer dynamics simulations are carried out using the Tully's fewest-switches surface-hopping approach based on the time-domain time-dependent density functional theory (TD-DFT) method.[1-3] The TD-DFT in the Kohn-Sham framework maps an interacting many-body system onto a system of noninteracting particles in which their electron densities equal to each other. As a result, the time-dependent charge density $\rho(r,t)$ of an interacting system is obtained from a set of time-dependent Kohn-Sham orbitals $\psi_p(r,t)$[4-6]

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

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

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

If expanding the total time-dependent electron or hole wavefunction $\psi_p(r,R,t)$ of a system in terms of interested unoccupied or occupied adiabatic Kohn-Sham orbitals $\phi_k(r,R)$ calculated from the DFT calculations along an adiabatic molecular dynamics trajectory

$$\psi_p(r,t) = \sum_k c_k(t)\phi_k(r;R) \quad (3)$$

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

$$i\hbar\frac{\partial c_j(t)}{\partial t} = \sum_k c_k(t)(\varepsilon_k\delta_{jk} - i\hbar d_{jk}) \quad (4)$$

where ε_k is the energy of the *k*th adiabatic state and d_{jk} is the nonadiabatic coupling between adiabatic states *j* and *k*. The former is directly obtained from the DFT calculations and the latter is calculated numerically through the finite difference method as the overlap integrals of relevant adiabatic states at times *t* and

$t + \Delta t$:

$$d_{jk} = \langle \phi_j(r;R) | \frac{\partial \phi_k(r;R)}{\partial t} \rangle \approx \frac{\langle \phi_j(t) | \phi_k(t+\Delta t) \rangle - \langle \phi_j(t+\Delta t) | \phi_k(t) \rangle}{2\Delta t} \quad (5)$$

in which $\phi_j(t)$ and $\phi_k(t+\Delta t)$ are the wavefunctions of adiabatic states j and k at times t and $t + \Delta t$, respectively. These physical quantities are always calculated with the collinear DFT method in previous studies, which have demonstrated that this strategy works very well for materials systems without the significant spin-orbit coupling (SOC) effects.[7-10]

The widely used collinear DFT method cannot directly include SOC effects during the self-consistent field calculations. Instead, the two-component noncollinear DFT method should be invoked to include the SOC effects in the self-consistent field calculations, where the spin-orbit operator is added in the molecular Hamitonian.[11-14]

In the two-component noncollinear DFT calculations, an orbital ϕ_k is represented using two spinors, which naturally mix α and β components, i.e. φ_k^α and φ_k^β

$$\phi_k = \begin{pmatrix} \varphi_k^\alpha \\ \varphi_k^\beta \end{pmatrix} \quad (6)$$

In such scheme, numerical calculations of d_{jk} are performed with the two-component spinors. The corresponding overlap integrals in Eq. 7 are calculated as dot products of the two-component spinors

$$\langle \phi_j(t) | \phi_k(t+\Delta t) \rangle = \begin{pmatrix} \varphi_j^\alpha(t) & \varphi_j^\beta(t) \end{pmatrix} \begin{pmatrix} \varphi_k^\alpha(t+\Delta t) \\ \varphi_k^\beta(t+\Delta t) \end{pmatrix}$$

$$= \langle \varphi_j^\alpha(t) | \varphi_k^\alpha(t+\Delta t) \rangle + \langle \varphi_j^\beta(t) | \varphi_k^\beta(t+\Delta t) \rangle. \quad (7)$$

To our best knowledge, only one work reports such kind of algorithm using the two-component noncollinear DFT method with the plane wave basis sets.[15] Differently, in this work, we have implemented it with much localized pseudo atomic orbitals in a locally modified OPENMX3.9 package.[16-18] The present developments will establish a useful simulation tool for simulating photoinduced nonadiabatic carrier processes of materials systems in which the SOC effects are not negligible, such as those Pb-containing perovskites.

Carrier Transfer Analysis

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

$$D_{\mu\nu i}(t) = D_{\mu\nu i}^{\alpha}(t) + D_{\mu\nu i}^{\beta}(t) = p_i(t)(\chi_{\mu i}^{\alpha}\chi_{\nu i}^{\alpha*} + \chi_{\mu i}^{\beta}\chi_{\nu i}^{\beta*}) \quad (8)$$

in which $p_i(t)$ is the time-dependent occupation number of the ith adiabatic state calculated on the basis of the above expanding coefficients $c_i(t)$; $\chi_{\mu i}^{\alpha}$ and $\chi_{\mu i}^{\beta}$ are the μth alpha and beta atomic orbital coefficients of the ith adiabatic state. Similar to the Mulliken charge analysis method,[19] we have then defined a population matrix P using the density matrix D and atomic overlap matrix S

$$P_{\mu\nu i} = D_{\mu\nu i}S_{\mu\nu} \quad (9)$$

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

$$P_a = \sum_i \left(\sum_{\mu\in a,\nu\in a} P_{\mu\nu i} + \frac{1}{2}\left(\sum_{\mu\in a,\nu\notin a} P_{\mu\nu i} + \sum_{\mu\notin a,\nu\in a} P_{\mu\nu i}\right)\right) \quad (10)$$

It should be noted that if only the one atomic orbital belongs to the ath atom, just half of $P_{\mu\nu i}$ is used, as done by the original Mulliken charge analysis method.[19] Accordingly, the total electron on a fragment A is done by summing all atomic charges belonging to that fragment

$$P_A = \sum_i p_i(t)P_{Ai} \quad (11)$$

in which

$$P_{Ai} = \sum_{\mu\in a}(\sum_{\mu\in a,\nu\in a}\left(\chi^{\alpha}_{\mu i}\chi^{\alpha*}_{\nu i} + \chi^{\beta}_{\mu i}\chi^{\beta*}_{\nu i}\right)S_{\mu\nu}) + \frac{1}{2}\sum_{a\in A}(\sum_{\mu\in a,\nu\notin a}\left(\chi^{\alpha}_{\mu i}\chi^{\alpha*}_{\nu i} + \chi^{\beta}_{\mu i}\chi^{\beta*}_{\nu i}\right)S_{\mu\nu} + \sum_{\mu\notin a,\nu\in a}(\chi^{\alpha}_{\mu i}\chi^{\alpha*}_{\nu i} + \chi^{\beta}_{\mu i}\chi^{\beta*}_{\nu i})\, S_{\mu\nu}) \quad (12)$$

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

$$dP_A = d(\sum_i c_i^* c_i P_{Ai}) = \sum_i (d(c_i^* c_i)P_{Ai} + c_i^* c_i dP_{Ai}) \quad (13)$$

in which the first term has a variational occupation for the adiabatic state i and the second term has a constant adiabatic state occupation but with changeable electron population. These two terms actually correspond to nonadiabatic and adiabatic 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 the atomic motion.

Additional Figures and Tables

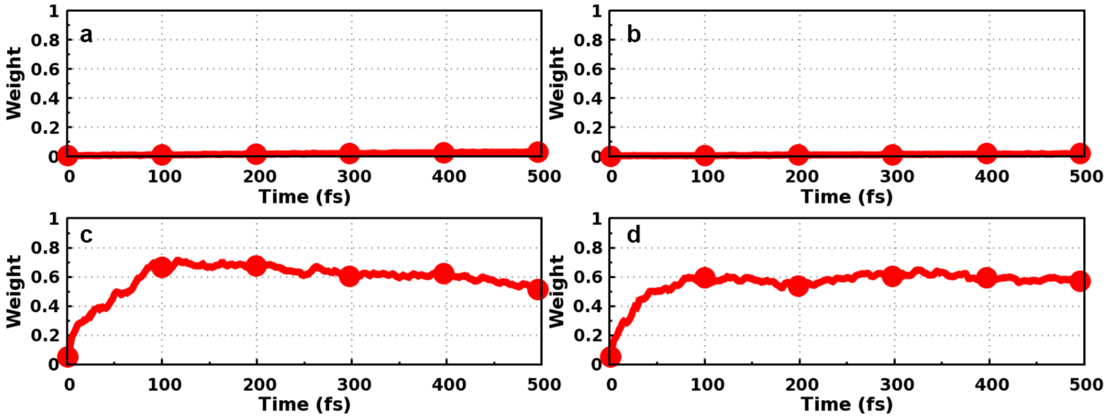

Figure S1: Time-dependent electron amounts transferred to either C_{60} (top, panel a and b) or C_{70} (bottom, panel c and d) from $MAPbI_3$ in nonadiabatic dynamics simulations using the iterated 4 ps (left, panel a and c) trajectory and 1 ps trajectory (right, panel b and d) respectively.

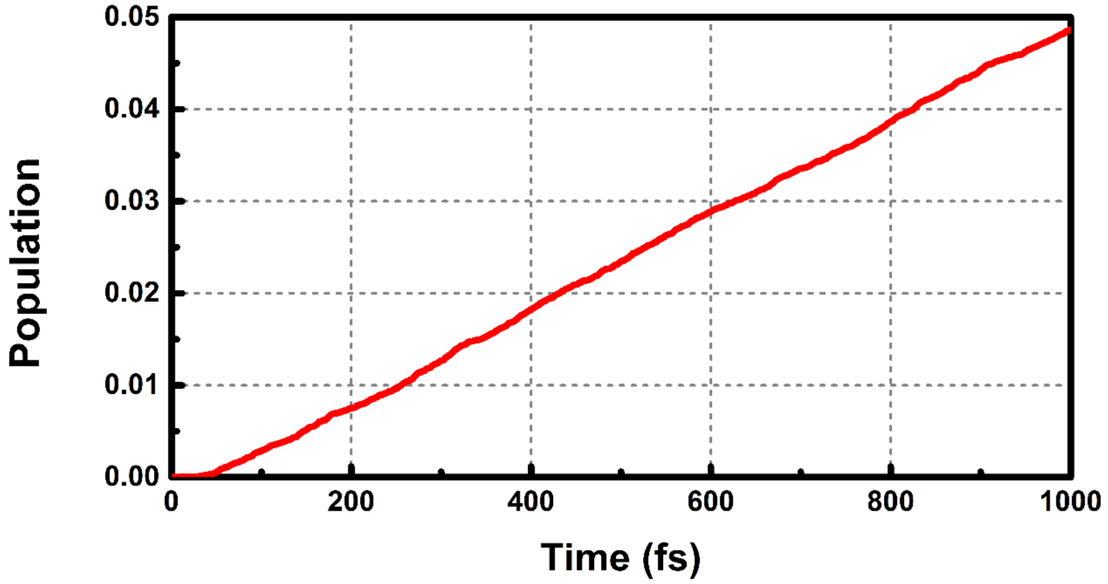

Figure S2: Time-dependent electron population on the first conduction band of C_{70} calculated based on the nonadiabatic dynamics.

The Relationship between the energy levels and the conduction bands

On the basis of the PDOS results calculated by the PBE+SOC and HSE06+SOC methods, as shown in Fig. 2, it can be found that: (1) In C60@MAPbI3, the lowest six unoccupied states belong to the first conduction band of C_{60}; and the 7th state is the CBM state of $MAPbI_3$; (2) in C70@MAPbI3, the first six unoccupied states belong to the first conduction band of C_{70}. However, due to the significant mixing between C_{70} and $MAPbI_3$, there are some tails on C_{70} for the CBM state of $MAPbI_3$ (see Fig. 3).

Table 1: Energy Differences (eV) between Relevant States Calculated with both the PBE+SOC+D3 and HSE06+SOC+D3 Methods.

C60@MAPbI3		
Energy gap (eV)	PBE+SOC+D3	HSE06+SOC+D3
$MAPbI_3$ CBM-C_{60} CBM	0.74	0.74
C_{60} CBM+1-$MAPbI_3$ CBM	0.32	0.51

C70@MAPbI3		
$MAPbI_3$ CBM-C_{70} CBM+1	0.24	0.19
C_{70} CBM+1-C_{70} CBM	0.44	0.52

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