

Non-adiabatic molecular dynamics study of exciton dissociation in Y6-based nonfullerene organic solar cells

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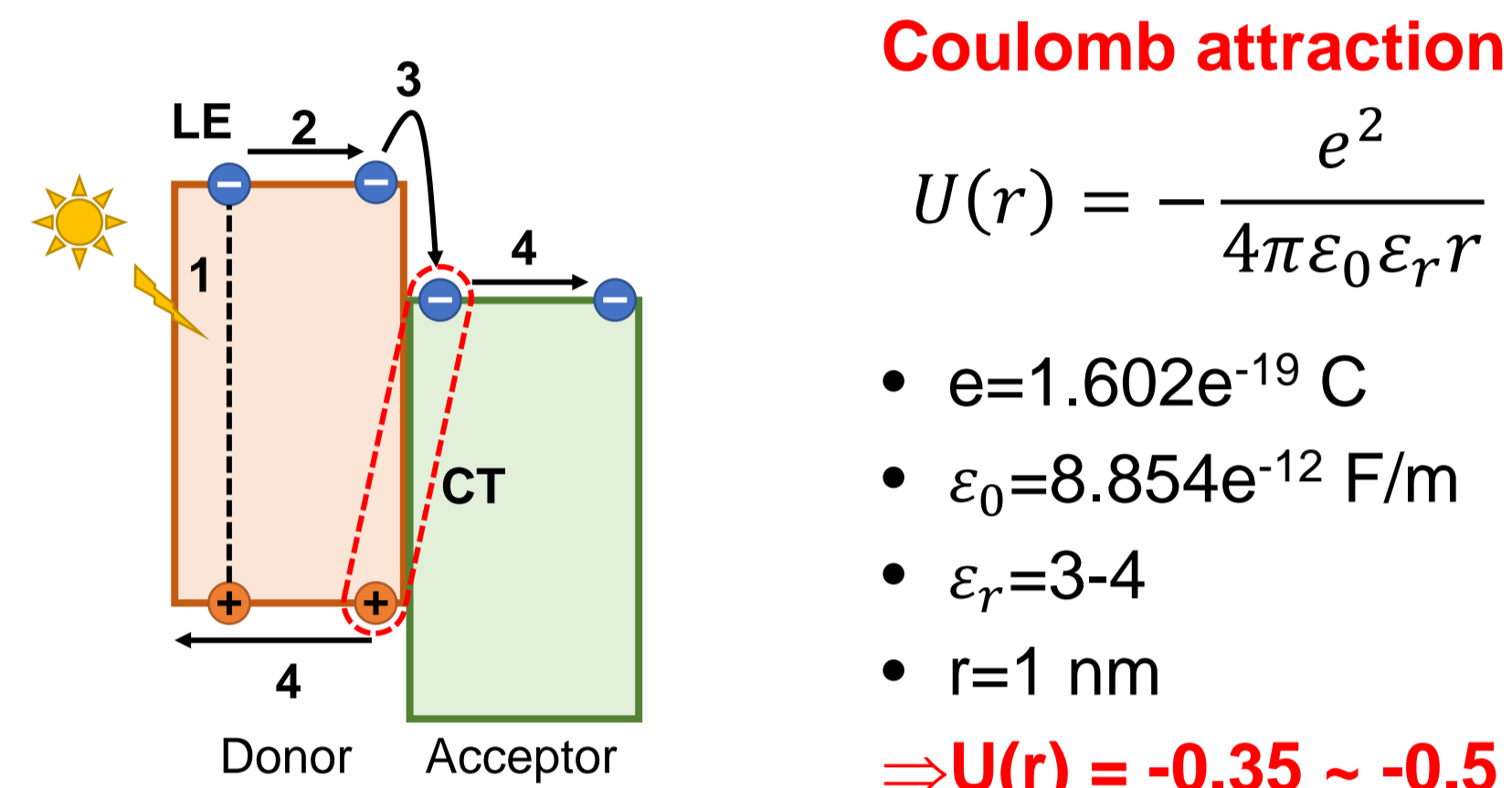
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Abstract

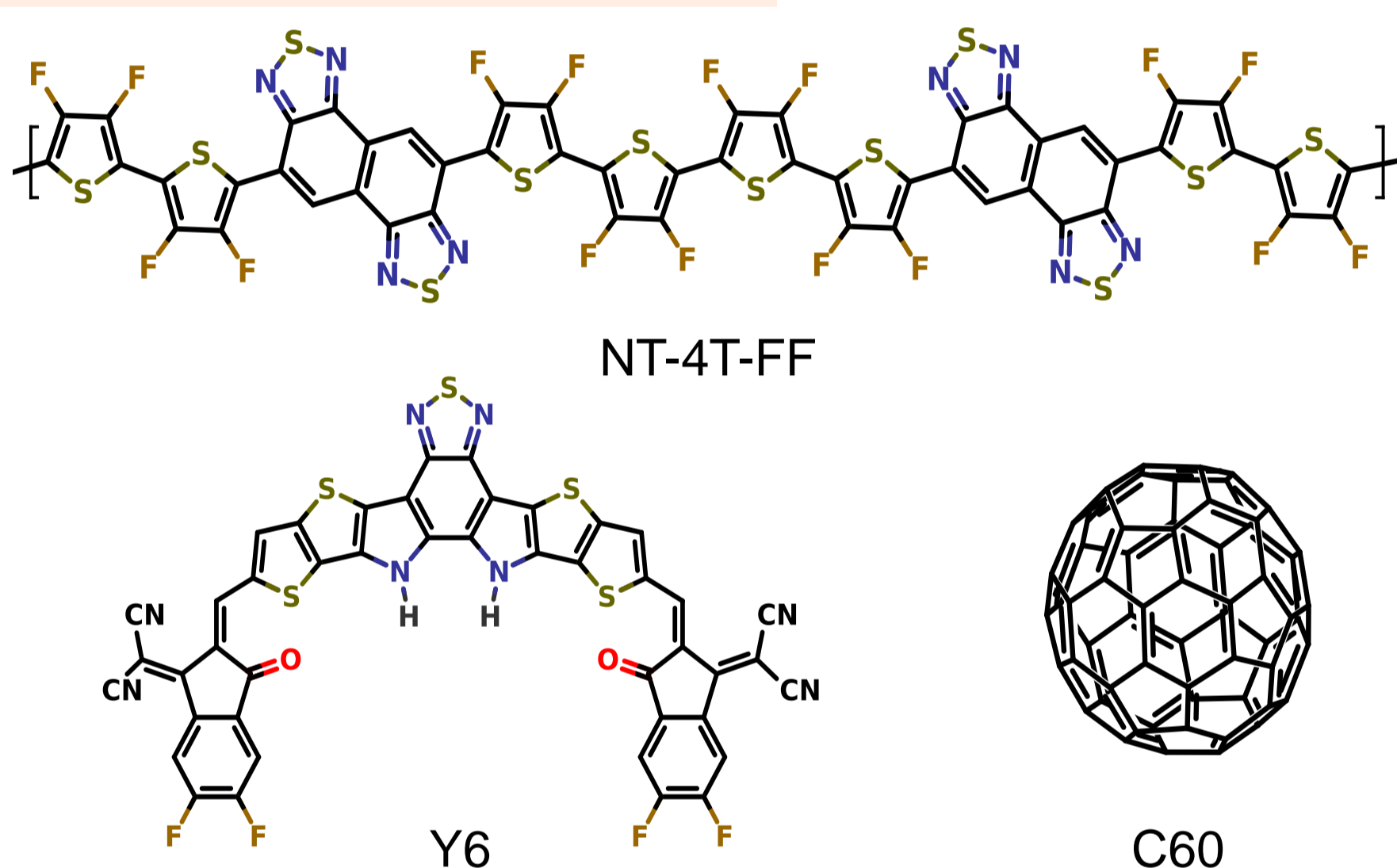
Y6-based nonfullerene organic solar cells (OSCs) have achieved an outstanding power conversion efficiency (PCE) of over 18% due to the low energy loss and efficient exciton dissociation with a very small energy offset. However, the exciton dissociation mechanism is under debate. It is still unclear why such small energy offset can result in sufficient exciton dissociation in nonfullerene systems but will lead to overwhelming charge recombination in fullerene systems. Here, we applied first-principles methods to study the charge transfer dynamics in both donor:Y6 and donor:C60 crystalline systems. Based on Ehrenfest molecular dynamics simulations, we proposed a five-step charge transfer process in nonfullerene system. We found that even with a small energy offset, the charge redistribution on both polymer backbone chain driven by Y6-induced dipole moment and Y6 backbone due to its intrinsic dipole moment can largely reduce Coulomb attraction of electron-hole pairs and thus facilitate exciton dissociation. Our study demonstrates that the dipole-driven charge redistribution and delocalization provide the driving force in Y6-based OSCs, which are missing in fullerene OSCs. Our study paves the way for developing next-generation OSC materials.

Introduction



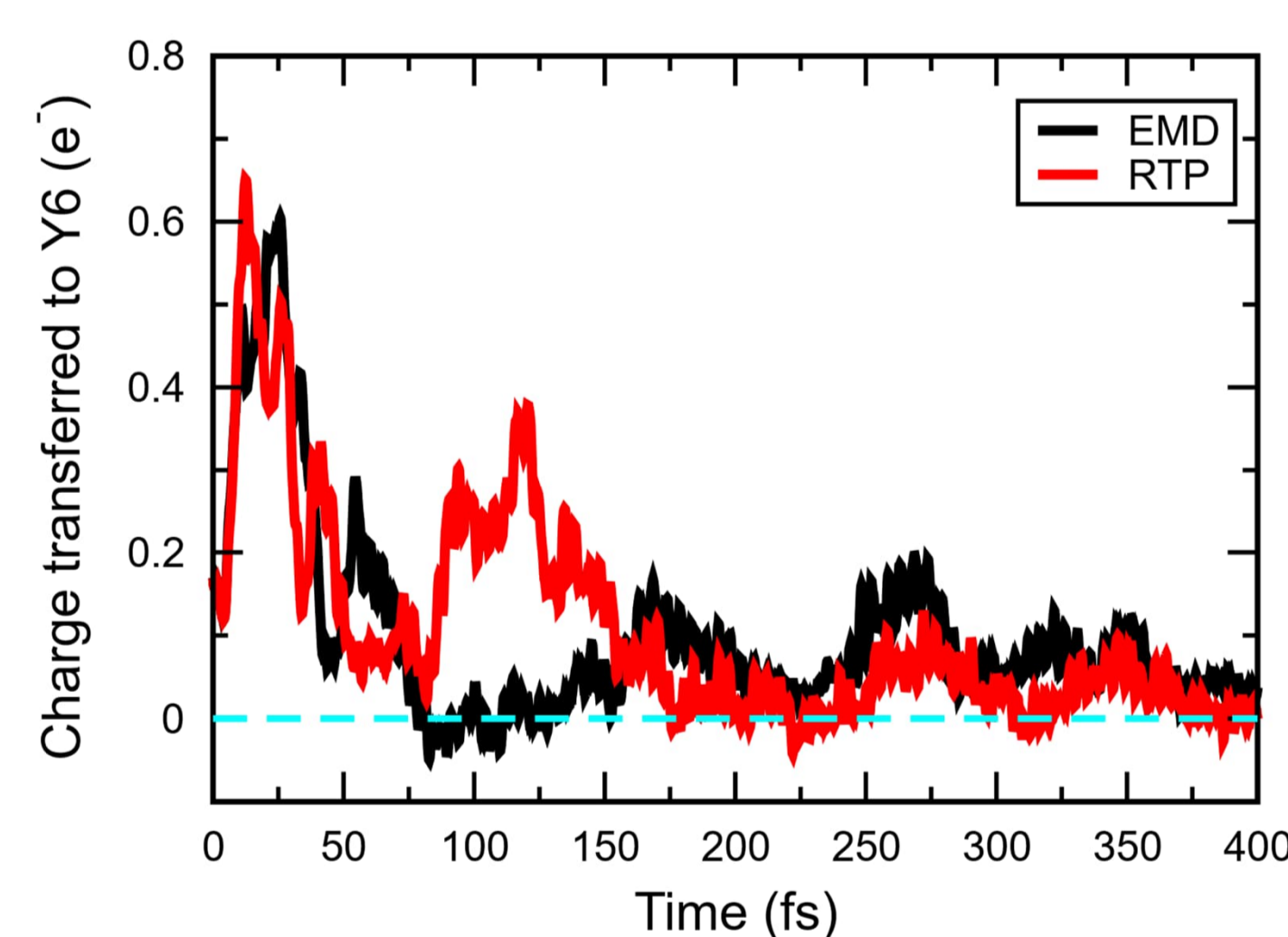
A driving force of 0.35 ~ 0.5 eV is necessary to overcome Coulomb attraction of electron-hole pairs in fullerene-based OSC devices.

Model systems



Two crystalline donor-acceptor dimer systems, NT-4T-FF:Y6 and NT-4T-FF:C60, with 3 dimensional periodic boundaries.

Thermal effect

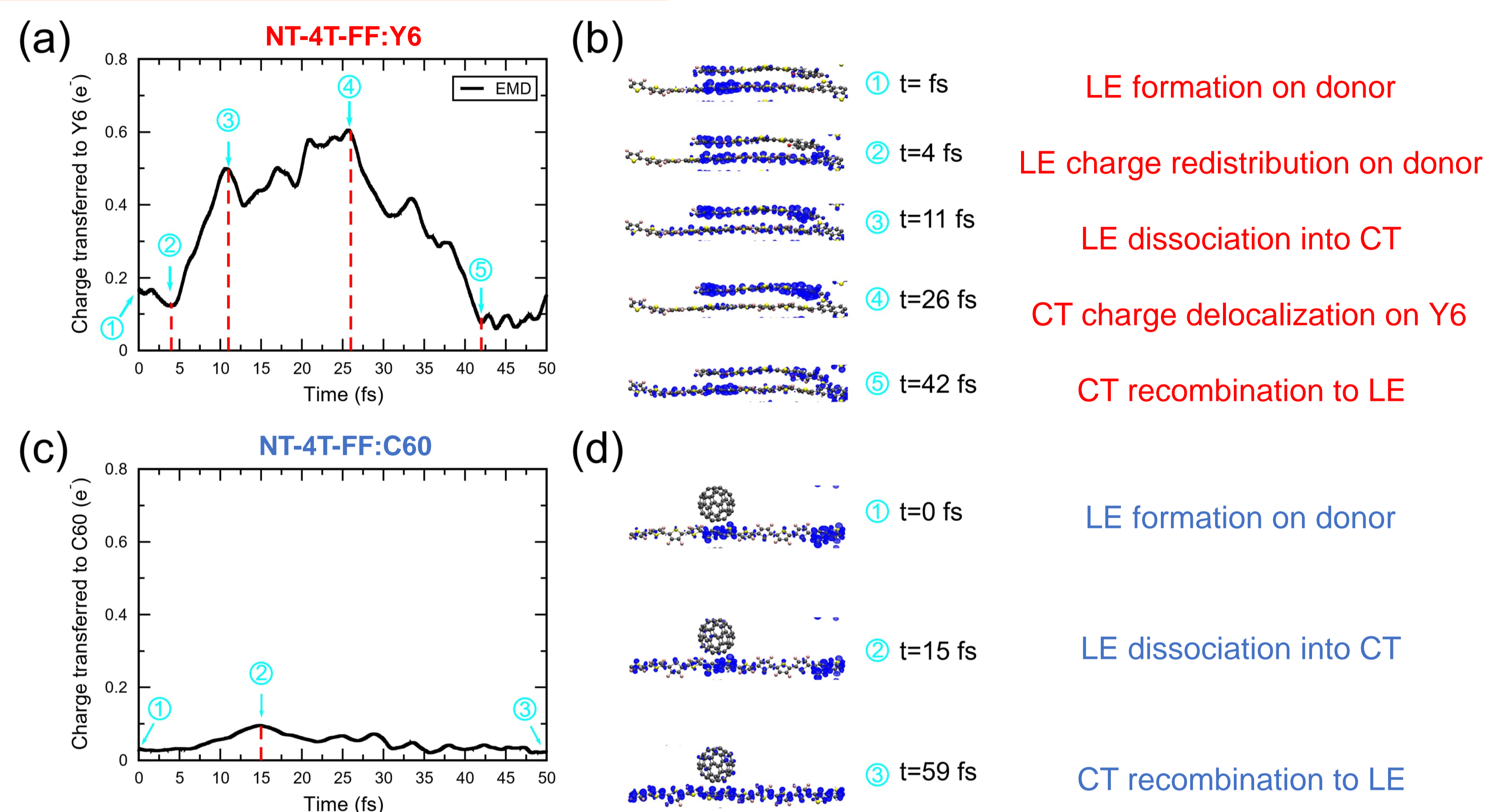


Thermal effect is not essential for exciton dissociation in NT-4T-FF:Y6 system with a small energy offset of 0.3 eV as indicated by the similar behavior of charge transfer dynamics after 150 fs in Ehrenfest MD (EMD) and Real-time Propagation (RTP) simulations.

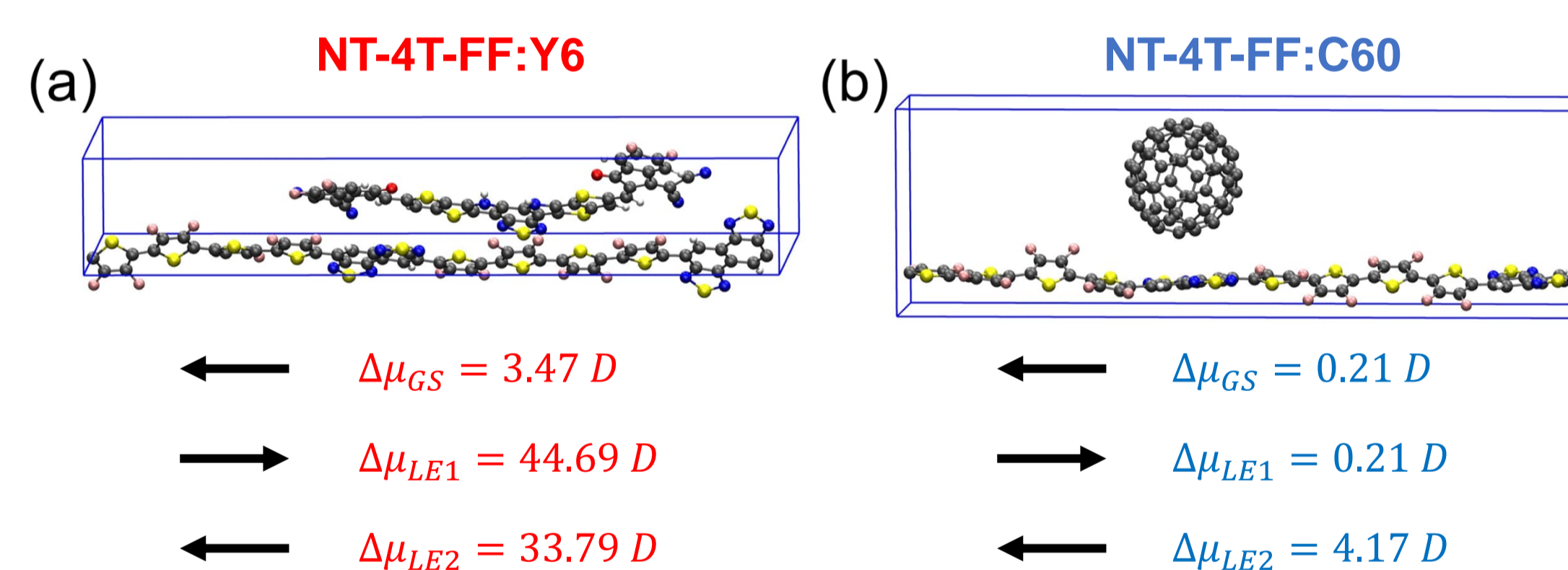
Method

- CP2K program package with a dual basis of Gaussian orbitals and plane waves, and GTH pseudopotentials
- Plane-wave density cutoff is 600 Ry, force tolerance is 0.01 eV/Å
- PBE-D3 exchange-correlation functional with DZVP-MOLOPT basis set
- NVT ensemble with T=300 K controlled by CSV thermostat is applied for BOMD, simulation duration is 15 ps with a time step of 0.5 fs.
- NVE ensemble with a time step of 2 as is applied for EMD and RTP simulations. Initial coordinates and velocities obtained from BOMD.
- Initial lowest-lying local exciton (LE1) state obtained by removing one electron from the polymer HOMO to the polymer LUMO.

Charge transfer process



Dipole moment effect



Maximally localized Wannier functions were applied to determine the coordinates of electrons and holes.

$$\Delta\mu_i = \mu_i(D/A) - \mu_i(D)$$

- $\Delta\mu_i$: the change on dipole moments along polymer w/ ($\mu_i(D/A)$) and w/o ($\mu_i(D)$) acceptor
- Black arrows: The direction of the change of dipole moment.
- i: ground state (GS), local exciton states (LE1, LE2)

The effect of Y6 on the dipole moment along polymer backbone at LE1 and LE2 is 1~2 orders of magnitude stronger than that of C60, which provides the driving force for charge redistribution along polymer backbone.

Charge transfer (CT) binding energy

$$E_b^{CT} = \sum_{d \in D^+, a \in A^-} \frac{q_d q_a}{4\pi\epsilon_0\epsilon_r r_{da}}$$

E_b^{CT} : CT exciton binding energy

$\epsilon_r = 4$: the relative dielectric constant

q_i : the charge of electrons and nuclei on donor (D^+) and acceptor (A^-)

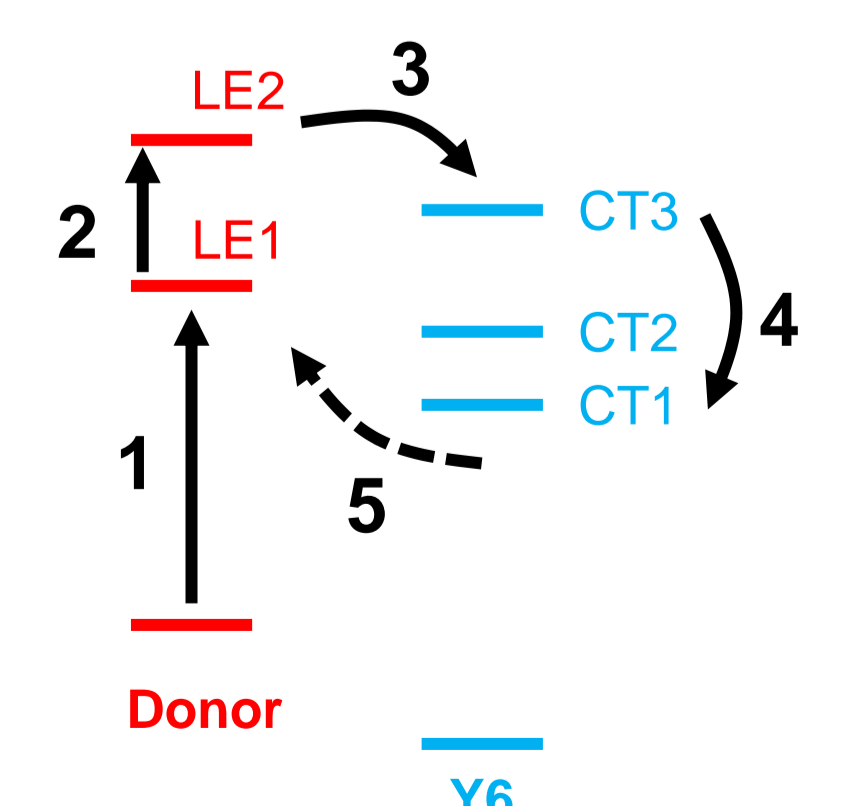
r_{da} : the distance between two charged particles locating on D^+ and A^- separately.

	E_b^{CT} (eV)	
State	NT-4T-FF:Y6	NT-4T-FF:C60
CT1	0.095	-0.29
CT2	-0.022	-0.296
CT3	0.143	-0.295

Y6 system adopts much weaker CT exciton binding energy than C60 system, favorable for CT exciton dissociation into free carriers.

Conclusion

- A five-step exciton dissociation model is proposed for Y6-based OSC devices.
- Dipole-driven charge redistribution on both polymer and Y6 backbones largely reduces Coulomb attraction of electron-hole pairs, facilitating efficient exciton dissociation under a small energy offset.
- Charge redistribution cannot be realized in C60-based OSC devices.



References

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- Cao, Z., et al. *J. Mater. Chem. A.* 2020, **8**, 20408-20413.

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