

Supporting Information: Polarized local excitons assist charge dissociation in Y6-based nonfullerene organic solar cells: a nonadiabatic molecular dynamics study

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Model system construction

We relaxed the NT-4T-FF:Y6 blend at the ground state using a periodic boundary condition along the polymer backbone. The lattice was adopted from the optimized repeating unit length of the polymer, and at least 20 Å of vacuum was applied along the y and z directions. To obtain the most stable ground-state structure, we tested five different configurations

by rotating the Y6 backbone around one IC ending group, which always stacks with one NT unit in NT-4T-FF. The results are shown in Figure S1(a). Previous studies^{1,2} have shown that Y6-based OSC blends prefer a face-on packing mode with π - π stacking through the electron-withdrawing units of both the polymer donor (NT units in NT-4T-FF) and the Y6 molecule (IC end groups in Y6). Figure S1(b) demonstrates that config2, after full structural relaxation, is the most stable configuration with the lowest total energy. To obtain the crystalline NT-4T-FF:Y6 structure, we further optimized the lattice constants of config2 along the y and z directions, as shown in Figure S2(b). Consequently, the unit cell dimensions for the crystalline NT-4T-FF:Y6 blend are $45.2 \text{ \AA} \times 22 \text{ \AA} \times 7.6 \text{ \AA}$. Figure S3(a) illustrates the structure of the crystalline NT-4T-FF:Y6 blend after fully thermal relaxation through a 15 ps BOMD simulation, reaching a converged total energy and temperature, as shown in Figure S3(b).

Figure S4 and S5 show the isosurface of molecular orbitals in the crystalline NT-4T-FF:Y6 blend, ranging from HOMO-3 (H-3) to LUMO+7 (L+7), obtained by a single-point DFT calculation at PBE and B3LYP levels, respectively. The molecular orbitals HOMO, LUMO+2, LUMO+4, and LUMO+6 are predominantly located within the NT-4T-FF polymer, while LUMO, LUMO+1, and LUMO+3 primarily reside on the Y6 acceptor molecule. In our electron excitation model, we assign the excitation of an electron from the HOMO of NT-4T-FF to higher unoccupied energy levels of NT-4T-FF as local excitons (LEs). The excitation from the HOMO of NT-4T-FF to higher unoccupied energy levels of the Y6 molecule is designated as charge transfer excitons (CTs). Figure S6 shows the energy diagram of the LE and CT excitons in the crystalline NT-4T-FF:Y6 blend obtained from a single-point DFT calculation at PBE and B3LYP levels, respectively. These diagrams serve as a reference for the subsequent EMD simulations. Following thermal relaxation, the energy difference between LE1 and CT1 is 0.27 eV, which is 0.06 eV larger than the offset prior to thermal relaxation. This increase can be attributed to the twisting of the backbone chains in both the NT-4T-FF polymer and the Y6 molecule.

In Figures S7 and S8, we conducted a comparison of the atomic and electronic structures of the Y6 molecule before and after the simplification of the side chain. Our analysis revealed that this simplification had a negligible impact on the atomic structure and orbital shapes of Y6. Although there was an overall upshift in the energy levels, the ordering remained unchanged (Table SI).

To investigate the influence of initial atomic configurations on excited state dynamics, we randomly picked up two more atomic configurations from the BOMD simulations to compare their electronic structures in Figures S9 and S10. We found that the energy levels and orbital shapes varied slightly with the different atomic configurations, suggesting a negligible effect of initial configurations on excited state dynamics (see Table SII). Our findings are consistent with Miyamoto et al.'s previous study, where they found that four different atomic configurations had similar excited state transitions.³

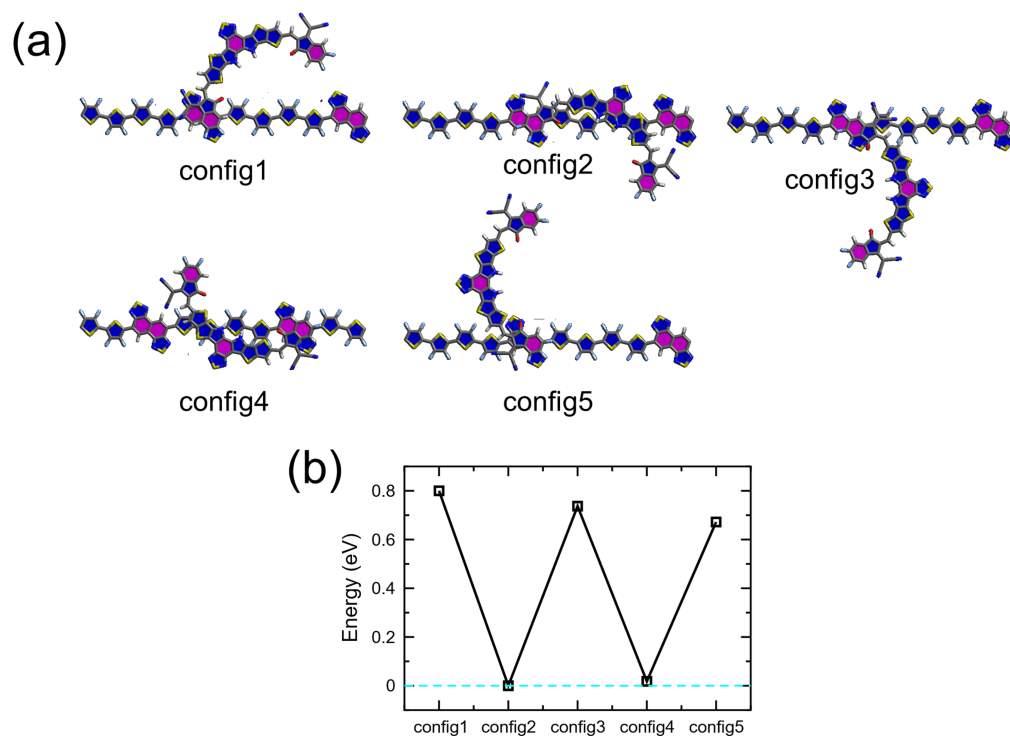


Figure S1: (a) Five configurations of the NT-4T-FF:Y6 blend obtained by rotating the Y6 backbone around one IC ending group stacking on one NT unit in NT-4T-FF. (b) Total energies after structural relaxation.

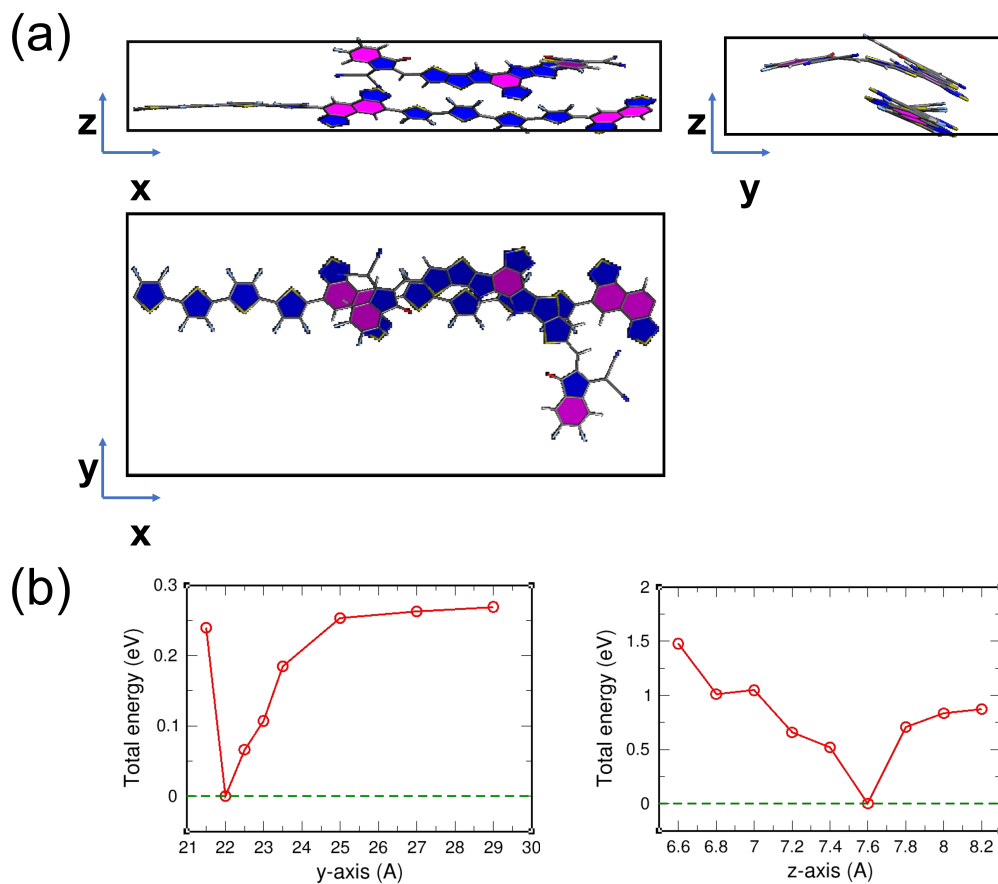


Figure S2: (a) Three views of the optimized crystalline NT-4T-FF:Y6 structure. (b) Optimization of the lattice constants along the y and z axes in the crystalline NT-4T-FF:Y6 blend.

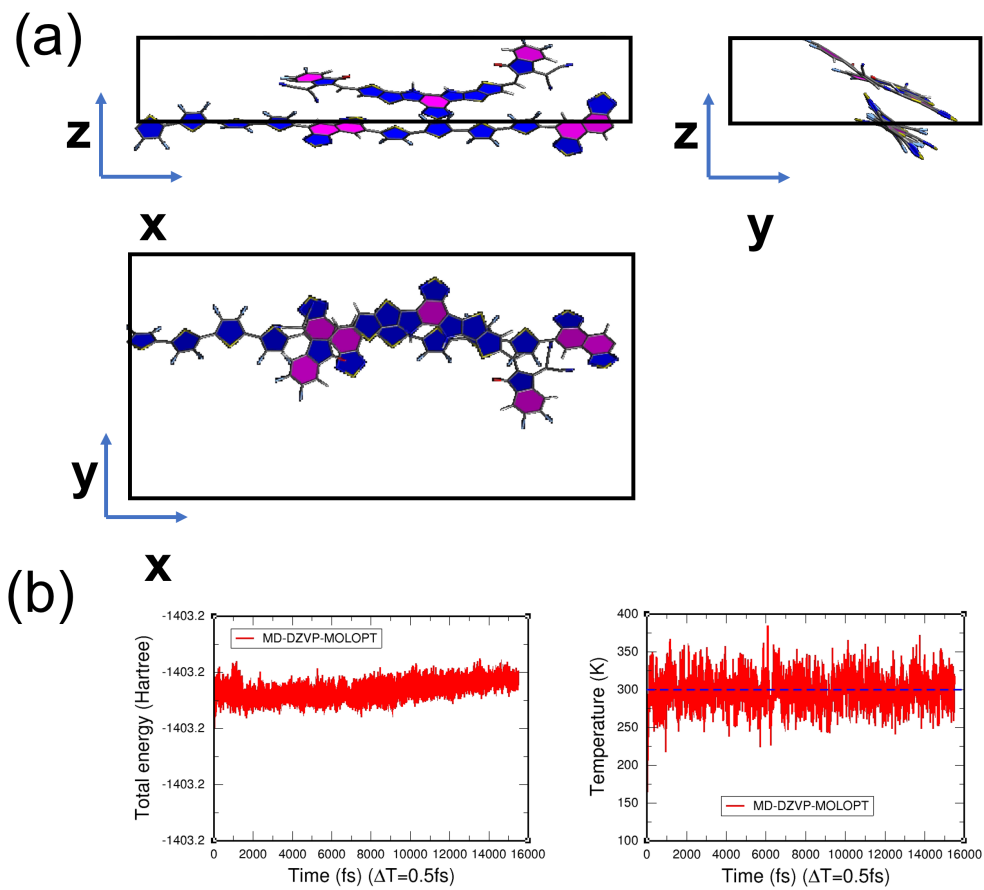


Figure S3: (a) Three views of the crystalline NT-4T-FF:Y6 structure after a 15 ps BOMD simulation. (b) Time evolution of total energy and temperature in the BOMD simulation.

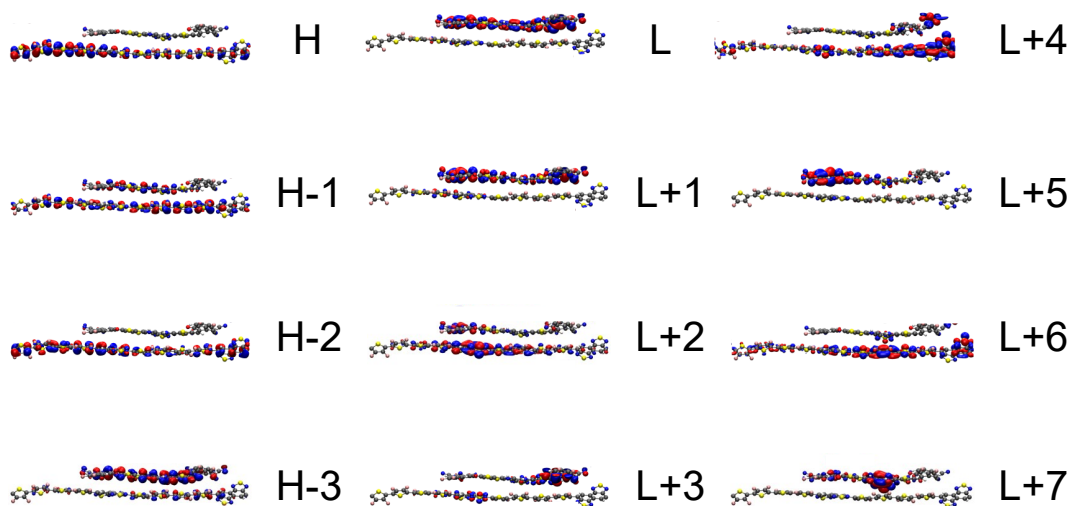


Figure S4: Isosurfaces of molecular orbitals ranging from HOMO-3 (H-3) to LUMO+7 (L+7) in the crystalline NT-4T-FF:Y6 blend calculated at PBE level.

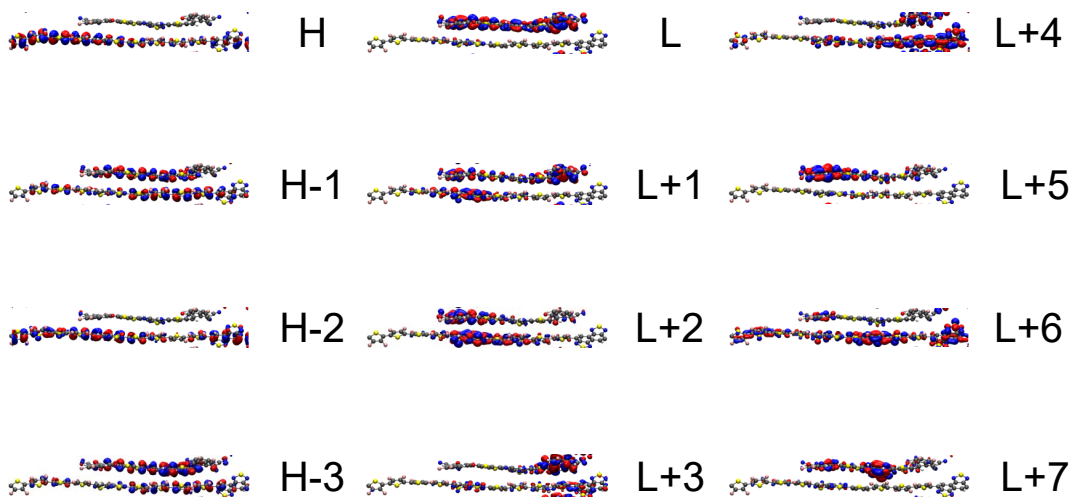


Figure S5: Isosurfaces of molecular orbitals ranging from HOMO-3 (H-3) to LUMO+7 (L+7) in the crystalline NT-4T-FF:Y6 blend calculated at the B3LYP level.

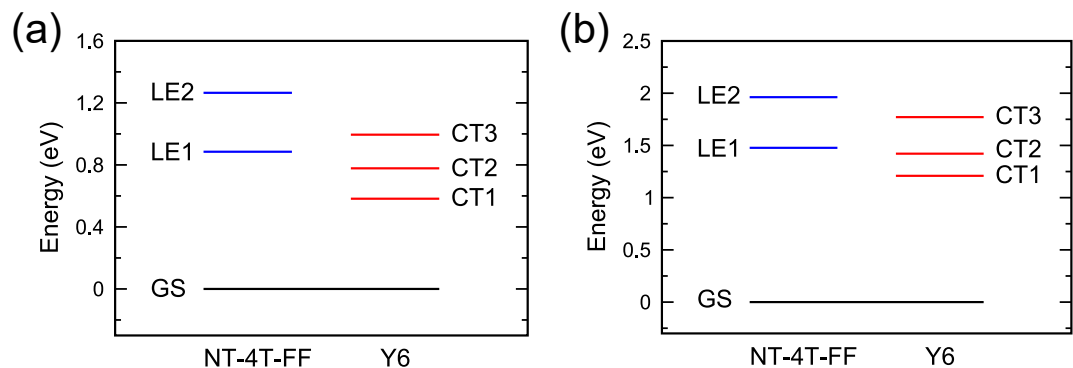


Figure S6: Energy diagram for the LE and CT excitons in one crystalline NT-4T-FF:Y6 structure calculated at (a) PBE level and (b) B3LYP level. The ground state (GS) energy is set to 0.

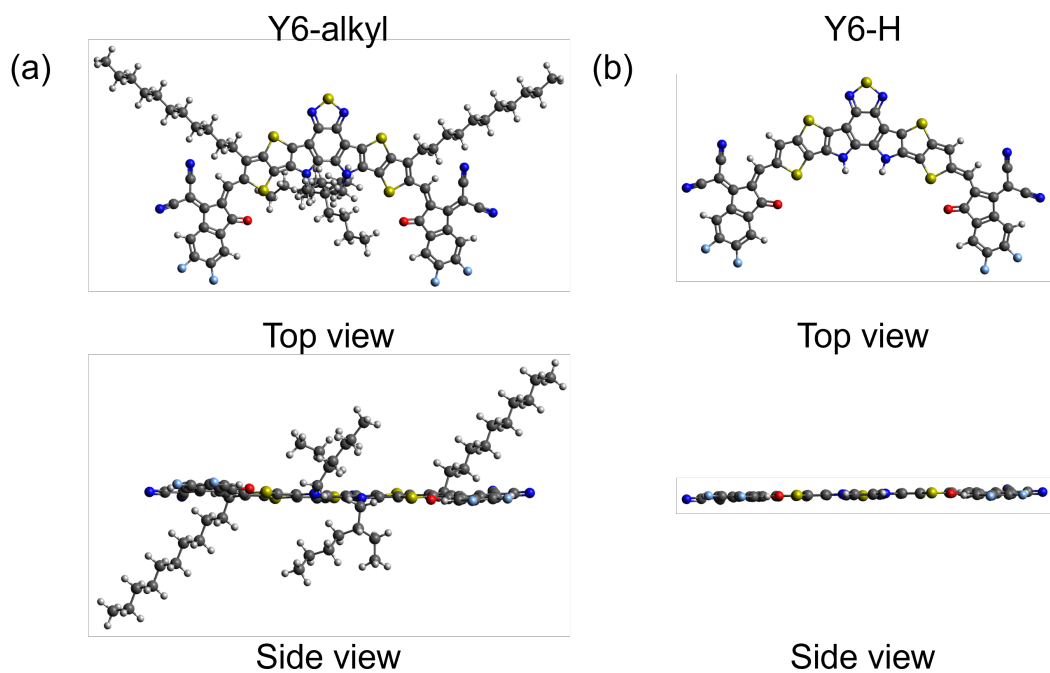


Figure S7: Top and side views of the optimized Y6 molecules (a) before (Y6-alkyl) and (b) after (Y6-H) the simplification.

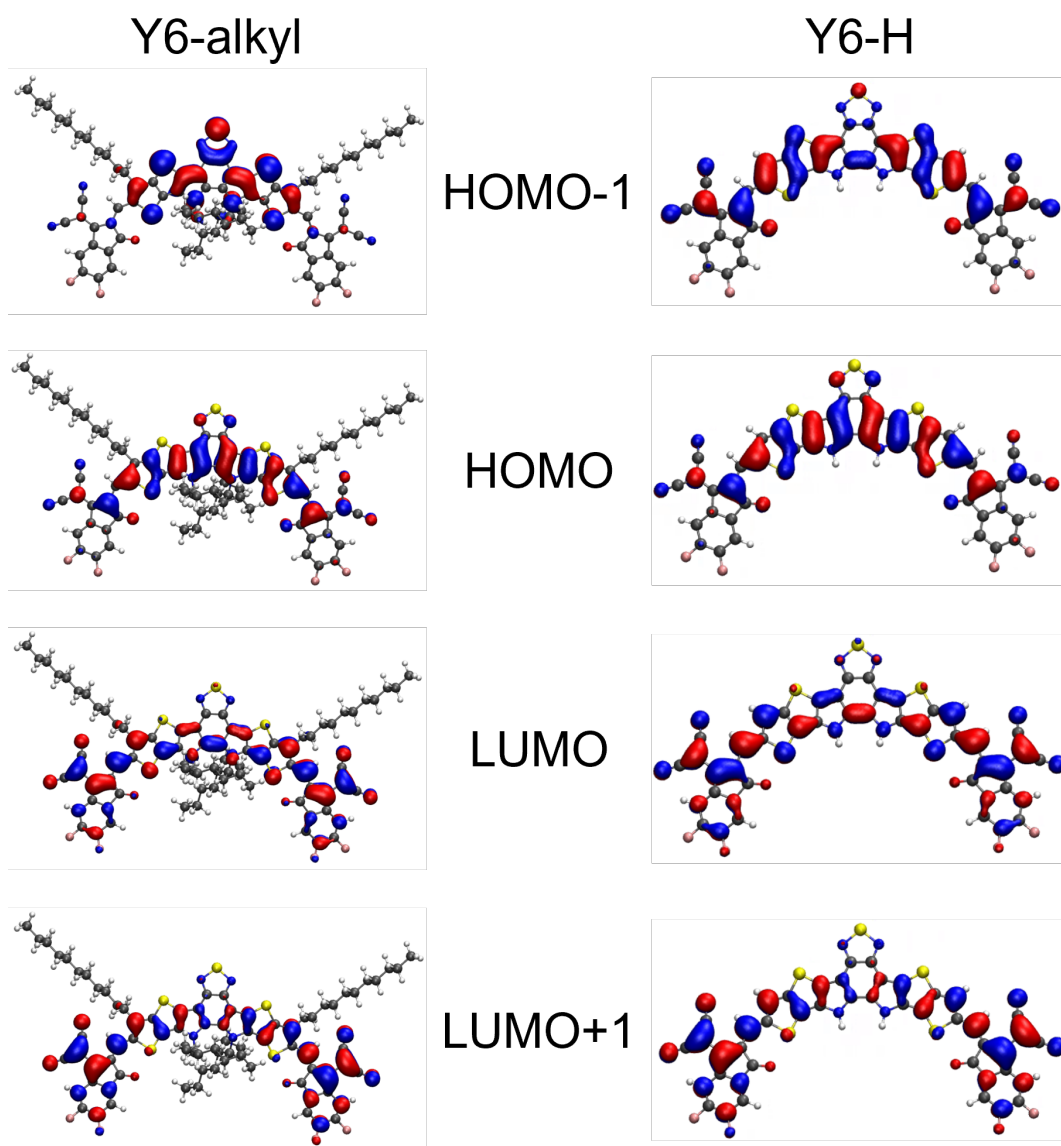


Figure S8: Isosurfaces of molecular orbitals ranging from HOMO-1 to LUMO+1 for the optimized Y6 molecules before (Y6-alkyl, left panel) and after (Y6-H, right panel) simplification.

Table SI: Energy levels from HOMO-1 to LUMO+1 calculated at the B3LYP level for the optimized Y6 molecules before (Y6-alkyl) and after (Y6-H) simplification (unit: eV).

state	Y6-alkyl	Y6-H
HOMO-1	-6.295	-6.584
HOMO	-5.583	-5.796
LUMO	-3.855	-4.014
LUMO+1	-3.575	-3.735

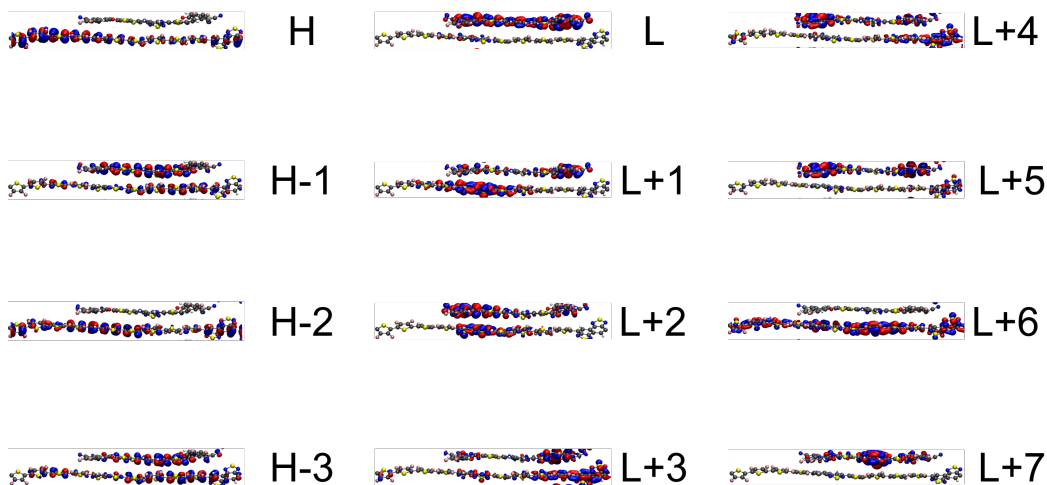


Figure S9: Isosurfaces of molecular orbitals ranging from HOMO-3 (H-3) to LUMO+7 (L+7) for configuration-2 structure calculated at the B3LYP level.

Table SII: The energy diagrams from HOMO to LUMO+4 calculated at the B3LYP level in three different NT-4T-FF:Y6 configurations obtained from BOMD simulations. The HOMO level energy is set to 0. configuration-1 is used for Ehrenfest molecular dynamics in the main text.

State (eV)	Configuration-1	Configuration-2	Configuration-3
HOMO	0	0	0
LUMO	1.209	1.319	1.19
LUMO+1	1.421	1.515	1.408
LUMO+2	1.477	1.605	1.464
LUMO+3	1.771	1.952	1.744
LUMO+4	1.962	2.055	1.915

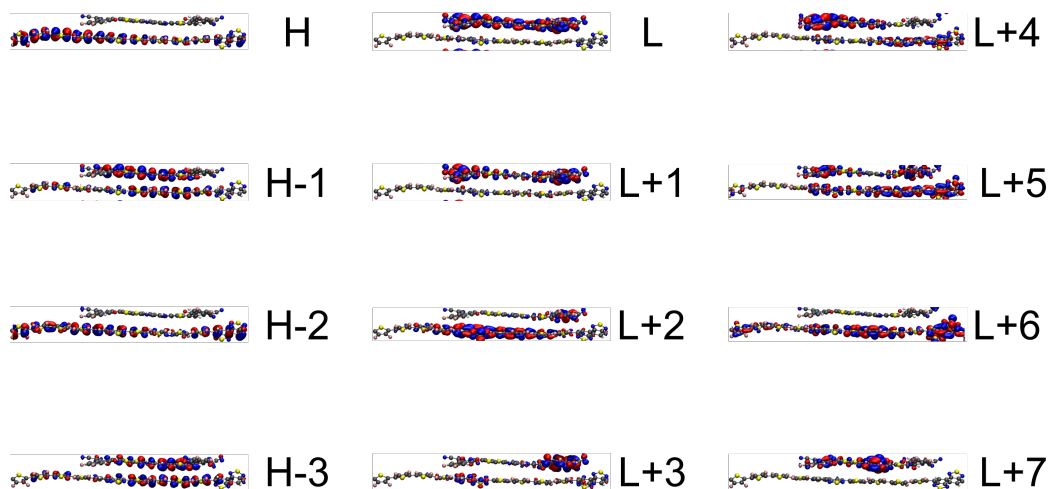


Figure S10: Isosurfaces of molecular orbitals ranging from HOMO-3 (H-3) to LUMO+7 (L+7) for configuration-3 structure calculated at the B3LYP level.

References

- (1) Han, G.; Guo, Y.; Ma, X.; Yi, Y. Atomistic Insight Into Donor/Acceptor Interfaces in High-Efficiency Nonfullerene Organic Solar Cells. *Solar RRL* **2018**, *2*, 1800190.
- (2) Cao, Z.; Yang, S.; Wang, B.; Shen, X.; Han, G.; Yi, Y. Multi-channel exciton dissociation in D18/Y6 complexes for high-efficiency organic photovoltaics. *Journal of Materials Chemistry A* **2020**, *8*, 20408–20413.
- (3) Miyamoto, Y.; Tateyama, Y.; Oyama, N.; Ohno, T. Conservation of the pure adiabatic state in Ehrenfest dynamics of the photoisomerization of molecules. *Scientific reports* **2015**, *5*, 18220.