Electronic Supplementary Information

Photoinduced Intra- and Inter-molecular Charge Transfer Dynamics in Organic Small Molecules with Intra-molecular Push-pull Electronic Structure

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1. Parameter details:

In all simulations, unless otherwise specified, the values of model parameters are set as $t_0 = 2.5\text{ eV}$, $\alpha = 41.0\text{ eV/nm}$, $K = 2100\text{ eV/nm}$, $M = 1.35 \times 10^5\text{ eV} \cdot \text{fs}^2/\text{nm}^2$, $t_1 = t_2 = 0.05\text{ eV}$, $t_3 = 0.1\text{ eV}$, and $U = 1.5\text{ eV}$. The intra-molecular offsite Coulomb interaction strength $V_{\parallel}$ and the inter-molecular vertical-neighbor sites Coulomb interaction strength $V_{\perp}$ are treated as Ohno potentials $V_{\parallel(\perp)} = U / \sqrt{1 + \kappa (r_{\parallel(\perp)}/a)^2}$ with $\kappa = 2$, $r_{\parallel} = a$, and $r_{\perp} = 3\text{ Å}$ ($\kappa$ is the screening factor, $a = 1.22\text{ Å}$ the average nearest-neighbor lattice constant, and $r_{\perp}$ the inter-molecular distance between vertical-neighbor sites). The inter-molecular electron hopping integral between vertical-
neighbor sites is described as $t_\perp = \frac{t_0}{10} \exp(1 - \frac{r}{5})$.

2. Iteratively solving the static equations:

Considering the electronic eigenstate $|\phi_{\mu,s}\rangle$, we can expand it on the Wannier basis, that is, $|\phi_{\mu,s}\rangle = \sum_n Z_{\mu,n,s} |n\rangle$. As such, the electronic eigenstates are obtained by solving the eigenequation of the electronic Hamiltonian, written as:

$$\left[U\left(\rho_{n,n,s} - \frac{1}{2}\right) + V_s \sum_s (\rho_{n+1,n+1} + \rho_{n-1,n-1} - 2)\right] Z_{\mu,n,s} + \left[t_1 Z_{\mu,1,s} + \Delta_{\mu} Z_{\mu,1,s}\right] \left[\delta\left(i\frac{10}{4}\right) + \delta\left(i\frac{12}{4}\right)\right]$$

$$+ \left[t_1 Z_{\mu,1,s} + \Delta_{\mu} Z_{\mu,1,s}\right] \left[\delta\left(i\frac{7}{4}\right) + \delta\left(i\frac{9}{4}\right)\right]$$

$$- \Delta_{\mu} Z_{\mu,1,s} - t_{n+1,n} Z_{\mu,n+1,s} - t_{n,n+1} Z_{\mu,n+1,s} = \epsilon_{\mu} Z_{\mu,n,s}$$

where $\mu$ and $\mu'$ represents the site index of central group and the site index of terminal groups, respectively. $\delta(x,\text{int})=1$, if $x=\text{int}$; and $\delta(x,\text{int})=0$, if $x \neq \text{int}$, where “int” means an integer.

On the other hand, by minimizing the total energy of the molecule, we can obtain the lattice balance equation:

$$u_{n+1} - u_n = \frac{2\alpha}{K} \left(\frac{1}{N-1} \sum_{s} \rho_{n,n+1,s} - \sum_s \rho_{n,n+1,s}\right)$$

where a fixed boundary is employed. $N$ is the total site number of a NFA molecule.

3. The quantum nonadiabatic evolution method:

Before dynamical simulations, we assume that the system is in ground state. Once the femtosecond electric pump pulse (FEPP) $E(t)$ is turned on, the system will experience an evolution. By using a nonadiabatic evolution method,\textsuperscript{1,2} we can
separately obtain the temporal evolution of the electronic state \( \Psi_{\nu,s}(n,t) \) and the lattice displacement \( u_n(t) \) (i.e., nuclear motion). The evolution of an electronic state \( \Psi_{\nu,s}(n,t) \) depends on the time dependent Schrödinger equation:

\[
\frac{i\hbar}{\partial t} \Psi_{\nu,s}(n,t) = -t_{n,n+1} \Psi_{\nu,s}(n+1,t) - t_{n-1,n} \Psi_{\nu,s}(n-1,t) + t_3 \{ \Psi_{\nu,s}(i+3,t)[\delta \left( \frac{i-7}{4}, \mathrm{int} \right) + \delta \left( \frac{i-9}{4}, \mathrm{int} \right)] \\
+ \Psi_{\nu,s}(i-3,t)[\delta \left( \frac{i-10}{4}, \mathrm{int} \right) + \delta \left( \frac{i-12}{4}, \mathrm{int} \right)] \}
\]

(S3)

\[
+ \Delta_{on} \Psi_{\nu,s}(i,t) - \Delta'_{on} \Psi_{\nu,s}(i',t) + [U \left( \rho_{n,n-1} - \frac{1}{2} \right) \\
+ V_{\nu} (\rho_{n+1,n+1} + \rho_{n-1,n-1} - 2) + eE(t)] \Psi_{\nu,s}(n,t)
\]

\( \Psi_{\nu,s}(n,t) = \langle n | \Psi_{\nu,s}(t) \rangle \) is the projection of an electronic state \( | \Psi_{\nu,s}(t) \rangle \) on the Wannier state of site \( n \). The hopping integrals \( t_{n,n+1} \) between sites \( n \) and \( n+1 \) in terminal groups, \( \pi \)-bridges, and central group are separately described as:

\[
t_{n,n+1} = \begin{cases} 
    t_0 - \alpha(u_{n+1} - u_n) - t_i \cos \left( \frac{n\pi}{2} \right) & 1 \leq n \leq 7; 29 \leq n \leq 35 \\
    t_0 - \alpha(u_{n+1} - u_n) & 8 \leq n \leq 10; 26 \leq n \leq 28 \\
    t_0 - \alpha(u_{n+1} - u_n) + (-1)^{n+1} t_2 & 11 \leq n \leq 25 
\end{cases}
\]

(S4)

The density matrix \( \rho_{n,m} \) is defined as:

\[
\rho_{n,m}(t) = \sum_{\nu,s} \Psi_{\nu,s}^*(n,t) g_{\nu,s} \sum_{\nu',s'} \Psi_{\nu',s'}(m,t)
\]

(S5)

Here, \( g_{\nu,s} \) is a time-independent distribution function and determined by the initial occupation of the electronic state \( | \Psi_{\nu,s}(t) \rangle \).

For the lattice part, the nuclear motion is classically described by the Newtonian equation of motion:

\[
M \ddot{u}_n = -K(2u_n - u_{n+1} - u_{n-1}) + 2\alpha[\rho_{n,n+1} - \rho_{n,n-1}] \\
+ eE(t)[\rho_{n,n} - 1] - \lambda M \dot{u}_n
\]

(S6)

Equations S3 and S6 can be numerically solved by the Runge-Kutta method of order
eight with step-size control.\(^3\) In addition, a damping term is introduced in Equation S6 to describe the energy dissipation into the surrounding medium by a tuning a parameter \(\lambda=0.05\ \text{fs}^{-1}\).

4. Transition details of a single NFA molecule:

Fig. S1. Time evolutions of the electron occupation number \(F_{\mu}(t)\) on the six band-edge levels in a single NFA molecule by different peak transitions, where the electronic push-pull potentials are separately set as \(\Delta_{\text{on}}=0\ \text{eV}\) (a1-c1), \(\Delta_{\text{on}}=0.3\ \text{eV}\) (a2-c2), \(\Delta_{\text{on}}=0.6\ \text{eV}\) (a3-c3), and \(\Delta_{\text{on}}=0.9\ \text{eV}\) (a4-c4), respectively.
5. Selection for the electronic push-pull potential of an actual NFA molecule:

Fig. S2. Charge density difference $\Delta Q_n$ between the molecular excited state and ground state, separately calculated by model method (a) and Gaussian method (b-c).\textsuperscript{4}

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When the electronic push-pull potential of a NFA molecule is chosen as $\Delta_{on} = 0.6$ eV, we find that the charge density difference between the excited state and ground state ($\Delta Q_n = q_{n, \text{excited state}} - q_{n, \text{ground state}}$, where $q_n = e(\rho_{n,n} - 1)$) calculated by model method (see Fig. S2(a)) is basically consistent with that calculated by Gaussian method (see Fig. S2(b) for ITIC and S2(c) for Y6).\textsuperscript{4} Therefore, for an actual ITIC or Y6 molecule, the electronic push-pull potential is estimated to be about $\Delta_{on} = 0.6$ eV.

6. Higher-energy transition details of different NFA molecular aggregates:
Fig. S3. Time evolutions of the electron occupation number $F_\mu(t)$ on several band-edge levels in NFA molecules with A-to-A type J-aggregation (a1-b1), A-to-D type J-aggregation (a2-b2), and D-to-D type H-aggregation (a3-b3), where the second and third peak transitions are compared.

For the second peak transition, we find that electron transition $\epsilon_2 \rightarrow \epsilon_2^*$ takes place in A-to-A type J-aggregate at the initial photoexcitation stage, soon the transited electron on the higher-energy level $\epsilon_2^*$ transits to the lower-energy level $\epsilon_1^*$ through an ultrafast internal conversion process (see Fig. S3(a1)). However, for A-to-D type J-
aggregate and D-to-D type H-aggregate, $\varepsilon_3 \rightarrow \varepsilon_3^*$ and $\varepsilon_6 \rightarrow \varepsilon_6^*$ takes place (see Figs. S3(a2) and S3(a3)), respectively. For the third peak transition, we find that $\varepsilon_1 \rightarrow \varepsilon_3^*$ occurs in A-to-A type J-aggregate, $\varepsilon_2 \rightarrow \varepsilon_4^*$ occurs in A-to-D type J-aggregate, and $\varepsilon_3 \rightarrow \varepsilon_5^*$ occurs in D-to-D type H-aggregate.

7. Effect of the molecular electronic push-pull potential on the inter-CT relaxation process:

Fig. S4. Time evolutions of the inter-molecular transferred charge quantity $Q_{\text{inter}}(t)$ for the first peak transition with different values of $\Delta_{\text{on}}$ in A-to-D type J-aggregate (a) and D-to-D type H-aggregate (b).

References:


3 Brankin, R.; Gladwell, I.; Shampine, L. RKSUITE: Software for ODE IVPS.