# Electronic Supplementary Information

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

Yiwen Ji,[a] Lingxia Xu,[a] Xinyu Mu,[a] Wenjing Wang,*[b] and Kun Gao*[a]

[a.] *School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China*

[b.] *College of Physics and Electronic Engineering, Qilu Normal University, Jinan 250200, China*

*Corresponding E-mail: wwj8686@163.com (Wenjing Wang); gk@sdu.edu.cn (Kun Gao)

### 1. Parameter details:

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

## 2. Iteratively solving the static equations:

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

$$\begin{aligned}&\left[U\left(\rho_{n,n,-s}-\frac{1}{2}\right)+V_{/\!/}\sum_{s}\left(\rho_{n+1,n+1}+\rho_{n-1,n-1}-2\right)\right]Z_{\mu,n,s}\\&+\left[t_3 Z_{\mu,i-3,s}+\Delta_{\text{on}}Z_{\mu,i,s}\right]\left[\delta\left(\frac{i-10}{4},\text{int}\right)+\delta\left(\frac{i-12}{4},\text{int}\right)\right]\\&+\left[t_3 Z_{\mu,i+3,s}+\Delta_{\text{on}}Z_{\mu,i,s}\right]\left[\delta\left(\frac{i-7}{4},\text{int}\right)+\delta\left(\frac{i-9}{4},\text{int}\right)\right]\\&-\Delta'_{\text{on}}Z_{\mu,i',s}-t_{n-1,n}Z_{\mu,n-1,s}-t_{n,n+1}Z_{\mu,n+1,s}=\varepsilon_{\mu}Z_{\mu,n,s}\end{aligned}\tag{S1}$$

$i$ and $i'$ represents the site index of central group and the site index of terminal groups, respectively. $\delta\left(x,\text{int}\right)=1$, if $x$=int; and $\delta\left(x,\text{int}\right)=0$, 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:

$$u_{n+1}-u_{n}=\frac{2\alpha}{K}\left(\frac{1}{N-1}\sum_{n,s}\rho_{n,n+1,s}-\sum_{s}\rho_{n,n+1,s}\right)\tag{S2}$$

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) $E\left(t\right)$ is turned on, the system will experience an evolution. By using a nonadiabatic evolution method,[1,2] we can separately obtain the temporal evolution of the electronic state $\Psi_{v,s}(n,t)$ and the lattice displacement $u_n(t)$ (i.e., nuclear motion). The evolution of an electronic state $\Psi_{v,s}(n,t)$ depends on the time dependent Schrödinger equation:

$$\begin{aligned} i\hbar\frac{\partial\Psi_{v,s}(n,t)}{\partial t} &= -t_{n,n+1}\Psi_{v,s}(n+1,t)-t_{n-1,n}\Psi_{v,s}(n-1,t) \\ &\quad +t_3\{\Psi_{v,s}(i+3,t)[\delta\left(\frac{i-7}{4},\mathrm{int}\right)+\delta\left(\frac{i-9}{4},\mathrm{int}\right)] \\ &\quad +\Psi_{v,s}(i-3,t)[\delta\left(\frac{i-10}{4},\mathrm{int}\right)+\delta\left(\frac{i-12}{4},\mathrm{int}\right)]\} \\ &\quad +\Delta_{\mathrm{on}}\Psi_{v,s}(i,t)-\Delta'_{\mathrm{on}}\Psi_{v,s}(i',t)+[U\left(\rho_{n,n,-s}-\frac{1}{2}\right) \\ &\quad +V_{//}\left(\rho_{n+1,n+1}+\rho_{n-1,n-1}-2\right)+eE(t)]\Psi_{v,s}(n,t) \end{aligned} \tag{S3}$$

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

$$t_{n,n+1}=\begin{cases} t_0-\alpha(u_{n+1}-u_n)-t_1\cos(n\pi/2) & 1\le n\le 7; 29\le n\le 35 \\ t_0-\alpha(u_{n+1}-u_n) & 8\le n\le 10; 26\le n\le 28 \\ t_0-\alpha(u_{n+1}-u_n)+(-1)^{n+1}t_2 & 11\le n\le 25 \end{cases} \tag{S4}$$

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

$$\rho_{n,m}(t)=\sum_{v,s}\Psi^*_{v,s}(n,t)g_{v,s}\sum_{v,s}\Psi_{v,s}(m,t) \tag{S5}$$

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

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

$$\begin{aligned} M\ddot{u}_n &= -K(2u_n-u_{n+1}-u_{n-1})+2\alpha[\rho_{n,n+1}-\rho_{n,n-1}] \\ &\quad +eE(t)[\rho_{n,n}-1]-\lambda M\dot{u}_n \end{aligned} \tag{S6}$$

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 fs$^{-1}$.

## 4. Transition details of a single NFA molecule:

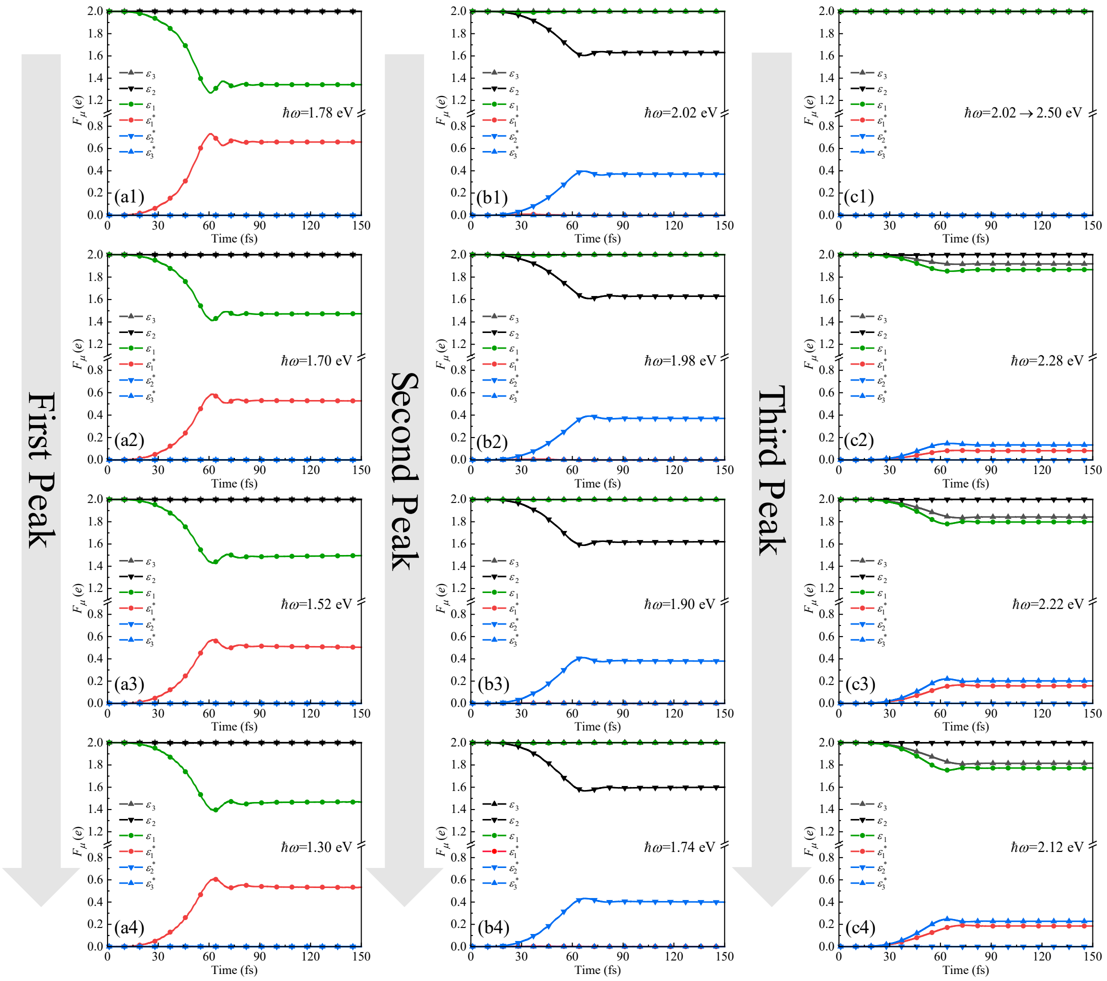

Fig. S1. Time evolutions of the electron occupation number $F_\mu(t)$ on the six band-edge levels in a single NFA molecule by different peak transitions, where the electronic push-pull potentials are separately set as $\Delta_{\text{on}}$=0 eV (a1-c1), $\Delta_{\text{on}}$=0.3 eV (a2-c2), $\Delta_{\text{on}}$=0.6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

## 5. Selection for the electronic push-pull potential of an actual NFA molecule:

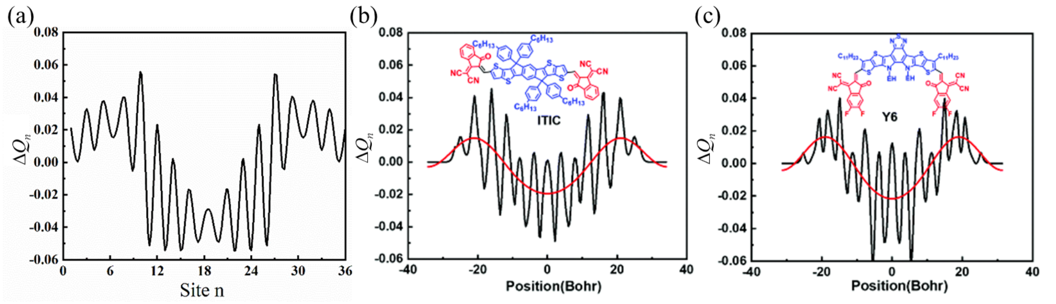

Fig. S2. Charge density difference $\Delta Q_n$ between the molecular excited state and ground state, separately calculated by model method (a) and Gaussian method (b-c).[4] Reproduced with permission from Chen et al., Chem. Soc. Rev. 49, 2828-2842 (2020). Copyright 2020 The Royal Society of Chemistry.

When the electronic push-pull potential of a NFA molecule is chosen as $\Delta_{\text{on}}$=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).[4] Therefore, for an actual ITIC or Y6 molecule, the electronic push-pull potential is estimated to be about $\Delta_{\text{on}} = 0.6\ \text{eV}$.

## 6. Higher-energy transition details of different NFA molecular aggregates:

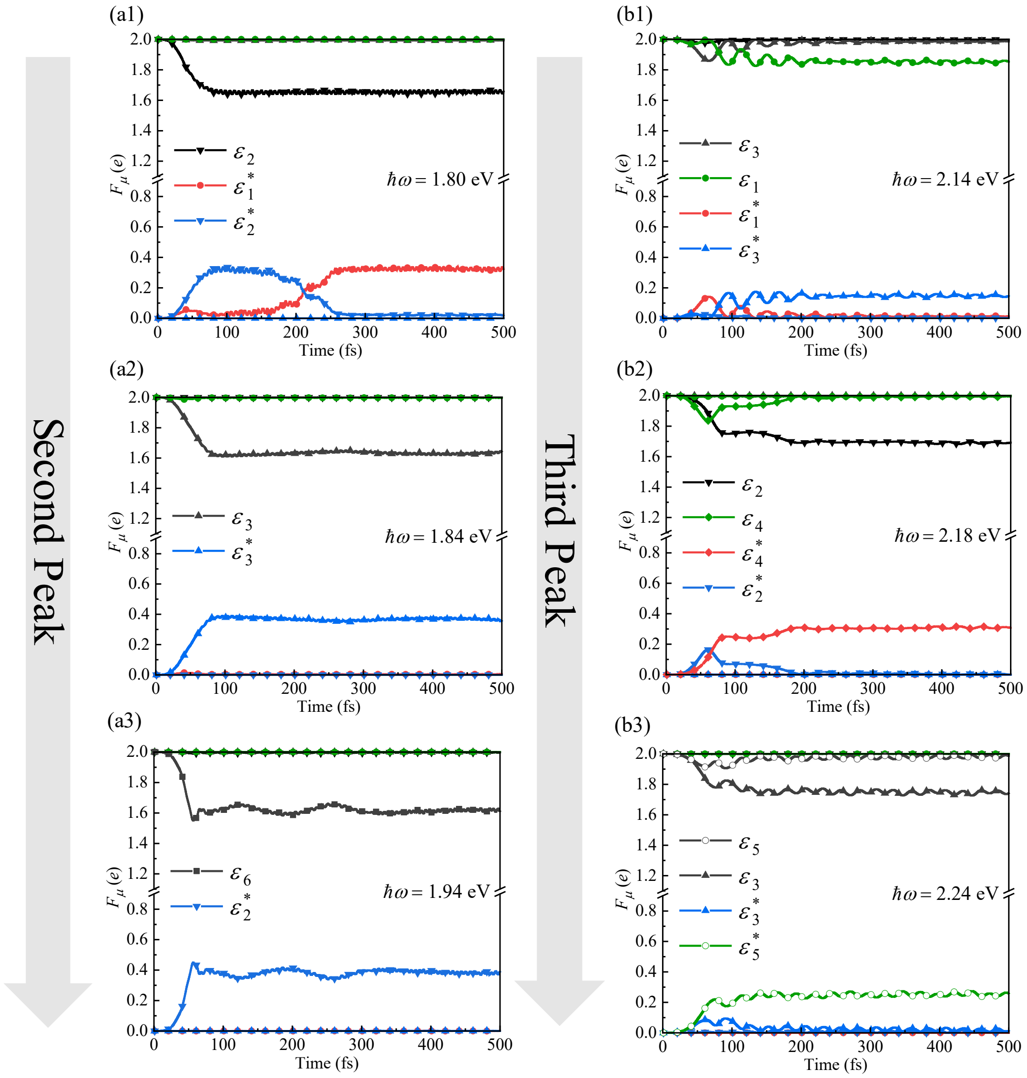

Fig. S3. Time evolutions of the electron occupation number $F_\mu\left(t\right)$ on several band-edge levels in NFA molecules with A-to-A type J-aggregation (a1-b1), A-to-D type J-aggregation (a2-b2), and D-to-D type H-aggregation (a3-b3), where the second and third peak transitions are compared.

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

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

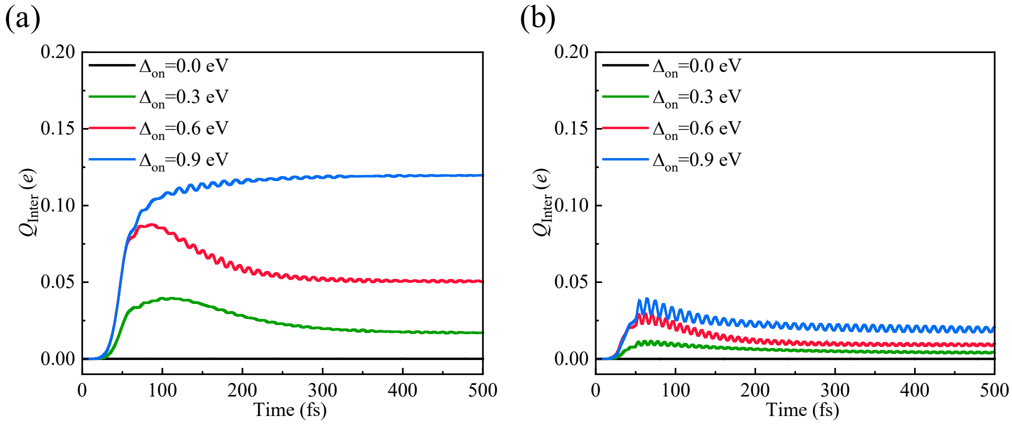

Fig. S4. Time evolutions of the inter-molecular transferred charge quantity $Q_{\mathrm{inter}}(t)$ for the first peak transition with different values of $\Delta_{\mathrm{on}}$ in A-to-D type J-aggregate (a) and D-to-D type H-aggregate (b).

## References:

1 Z. An, C. Q. Wu, and X. Sun, *Phys. Rev. Lett.* 2004, **93**, 216407.

2 Anders A. Johansson and Sven Stafström, *Phys. Rev. B* 2004, **69**, 235205.

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

4 X. Wan, C. Li, M. Zhang, and Y. Chen, *Chem. Soc. Rev.* 2020, **49**, 2828.