Supplementary Information

Quantum Dynamics of DNA Excited State Relaxation Driven by Base Stacking and Pairing Interactions

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In this Supplementary Information, we present the details of hierarchy equation of motion (HEOM), model and parameters and the detailed data treatment of population dynamics. The discrete variable representation (DVR) and population dynamics of other nucleobases have been described in details.

I. HIERARCHY EQUATION OF MOTION

The hierarchical equations of motion (HEOM) formalism provides a nonperturbative and numerically exact approach to treat quantum dissipative dynamics, especially in the strong system-bath coupling and low-temperature regimes [1, 2]. It is derived from the path-integral representation of the reduced density matrix with the Feynman-Vernon influence functional. We start from the path-integral expression for the reduced density matrix of a two-level system

$$\hat{\rho}(\bar{\psi},\psi';t) = \int \mathcal{D}\bar{\psi}\mathcal{D}\psi \int \mathcal{D}\bar{\psi}'\mathcal{D}\psi'\, \rho(\bar{\psi}_0,\psi_0';t_0)\, e^{\frac{i}{\hbar}S[\bar{\psi},\psi]}\, \mathcal{F}_{\mathrm{FV}}[\bar{\psi},\psi;\bar{\psi}',\psi']\, e^{-\frac{i}{\hbar}S[\bar{\psi}',\psi']}\,. \tag{S1}$$

The Feynman-Vernon influence functional is written as

$$\mathcal{F}_{\mathrm{FV}}[\cdot] = \exp\Bigg\{-\frac{1}{\hbar}\int_{t_0}^{t} ds \int_{t_0}^{s} ds'\, V_\times(s)\Big[V_\times(s')\coth\big(\tfrac{\beta\hbar\omega}{2}\big)\cos\omega(s-s') - iV_\circ(s')\sin\omega(s-s')\Big]\Bigg\}, \tag{S2}$$

with the abbreviations $V_\times(t) \equiv V(\bar{\psi}(t),\psi(t)) - V(\bar{\psi}'(t),\psi'(t))$ and $V_\circ(t) \equiv V(\bar{\psi}(t),\psi(t)) + V(\bar{\psi}'(t),\psi'(t))$. With introducing of the bath kernels

$$L_1(t) = \int_0^\infty d\omega\, J(\omega)\sin(\omega t), \tag{S3}$$

$$L_2(t) = \int_0^\infty d\omega\, J(\omega)\coth\Big(\frac{\beta\hbar\omega}{2}\Big)\cos(\omega t), \tag{S4}$$

we have

$$\mathcal{F}_{\mathrm{FV}} = \exp\Big(\tfrac{i}{\hbar}\iint V_\times(s)V_\circ(s')L_1(s-s') - \tfrac{1}{\hbar}\iint V_\times(s)V_\times(s')L_2(s-s')\Big).$$

For the Drude type of the spectral density, which shows

$$J(\omega) = \frac{\hbar\zeta}{\pi\omega_0}\frac{\gamma^2\omega}{\omega^2+\gamma^2}, \tag{S5}$$

we obtain the kernels evaluate to

$$L_1(t) = \frac{\hbar\zeta\gamma^2}{2\omega_0}\, e^{-\gamma t}, \tag{S6}$$

$$L_2(t) = \frac{\hbar\zeta\gamma^2}{2\omega_0}\Big\{ \cot\Big(\frac{\beta\hbar\gamma}{2}\Big) e^{-\gamma t} - \sum_{k=1}^{\infty} \frac{4}{\beta\hbar}\frac{\nu_k\gamma^2}{\nu_k^2-\gamma^2}\, e^{-\nu_k t}\Big\}, \tag{S7}$$

where $\nu_k = 2\pi k/(\beta\hbar)$ are the Matsubara frequencies. By defining the auxiliary time-dependent superfields, one obtains

$$\varphi(t) \equiv i\, V_\times(t), \tag{S8}$$

$$\Theta(t) \equiv i\frac{\zeta}{\beta\hbar\omega_0}\Big[-i\frac{\beta\hbar\gamma}{2} V_\circ(t) + \frac{\beta\hbar\gamma}{2}\cot\Big(\frac{\beta\hbar\gamma}{2}\Big) V_\times(t)\Big], \tag{S9}$$

$$\psi_k(t) \equiv i\frac{\zeta}{\beta\hbar\omega_0}\frac{2\gamma^2}{\nu_k^2-\gamma^2} V_\times(t). \tag{S10}$$

With these definitions, one obtains the factorized form

$$\mathcal{F}_{\mathrm{FV}} = \exp\Big(\int_{t_0}^{t} ds \int_{t_0}^{s} ds'\, \varphi(s)\Theta(s')\gamma e^{-\gamma(s-s')}\Big) \prod_{k=1}^{\infty} \exp\Big(\int_{t_0}^{t} ds \int_{t_0}^{s} ds'\, \varphi(s)\psi_k(s')\nu_k e^{-\nu_k(s-s')}\Big).$$

Introduce the auxiliary density operators (ADOs) by inserting powers of the integrals appearing above into the path integral:

$$\begin{aligned} \rho^{(n)}_{j_1,\ldots,j_K}(\bar\psi,\psi';t) = &\int \mathcal{D}\bar\psi\mathcal{D}\psi \int \mathcal{D}\bar\psi'\mathcal{D}\psi'\, \rho(\bar\psi_0,\psi_0';t_0)\, e^{\frac{i}{\hbar}S[\bar\psi,\psi]}\, \mathcal{F}_{\mathrm{FV}}[\cdot]\, e^{-\frac{i}{\hbar}S[\bar\psi',\psi']} \\ &\times \Big\{ e^{-\gamma t}\Big[-\int_{t_0}^{t} ds\, \gamma\Theta(s) e^{\gamma s}\Big]\Big\}^{n} \prod_{k=1}^{K} \Big\{ e^{-\nu_k t}\Big[-\int_{t_0}^{t} ds\, \nu_k\psi_k(s) e^{\nu_k s}\Big]\Big\}^{j_k}, \end{aligned} \tag{S11}$$

with nonnegative integers n, j_k. Differentiating the ADOs with respect to time and using the derivative of the exponential kernels, one yields the coupled hierarchy

$$\begin{aligned} \frac{\partial}{\partial t}\hat\rho_{j_0,j_1,\ldots,j_K}(t) = &-\Big[i\hat{\mathcal{L}}_s + \sum_{k=0}^{K} j_k\nu_k + \hat\Xi \Big]\, \hat\rho_{j_0,j_1,\ldots,j_K}(t) \\ &- \hat\varphi\, \hat\rho_{j_0+1,j_1,\ldots,j_K}(t) - \sum_{k=1}^{K} \hat\varphi\, \hat\rho_{j_0,j_1,\ldots,j_k+1,\ldots,j_K}(t) \\ &- j_0\nu_0\, \hat\Theta\, \hat\rho_{j_0-1,j_1,\ldots,j_K}(t) - \sum_{k=1}^{K} j_k\nu_k\, \hat\psi_k\, \hat\rho_{j_0,j_1,\ldots,j_k-1,\ldots,j_K}(t), \end{aligned} \tag{S12}$$

where $j_0 \equiv n$, $\nu_0 \equiv \gamma$, and $\hat{\mathcal{L}}_s(\cdot) = \frac{1}{\hbar}[\hat H_s, \cdot]$. The superoperators are given by

$$\hat\varphi \equiv i\, \hat V_\times, \tag{S13}$$

$$\hat\Theta \equiv i\frac{\zeta}{\beta\hbar\omega_0}\big[z\cot z\, \hat V_\times - iz\, \hat V_\circ \big], \qquad z \equiv \frac{\beta\hbar\gamma}{2}, \tag{S14}$$

$$\hat\psi_k \equiv i\frac{\zeta}{\beta\hbar\omega_0}\frac{2z^2}{\pi^2k^2 - z^2}\, \hat V_\times, \qquad \nu_k = \frac{2\pi k}{\beta\hbar}, \tag{S15}$$

$$\hat\Xi \equiv \frac{\zeta}{\beta\hbar\omega_0}\Big(1 - z\cot z\Big)\, \hat V_\times \hat V_\times. \tag{S16}$$

Here $\hat O_\times \hat X \equiv \hat O\hat X - \hat X\hat O$ and $\hat O_\circ \hat X \equiv \hat O\hat X + \hat X\hat O$. In numerical work the Matsubara product is truncated at some finite K by replacing the neglected tail by a short-time contribution, leading to a finite hierarchy. Increasing the depth $\sum_k j_k$ and K until observables converge ensures numerical accuracy.

II. DISCRETE VARIABLE REPRESENTATION (DVR) METHOD

The discrete variable representation (DVR) is a numerical method to solve the Schrödinger equation by discretizing the continuous position space into a finite grid. Instead of working directly in the infinite-dimensional Hilbert space, the wave function is projected onto a finite-dimensional subspace spanned by a set of grid-localized basis functions. This is achieved by starting with a chosen primitive basis $\{\phi_\alpha(x)\}_{\alpha=1}^N$ and performing an orthogonal transformation to a grid basis $\{\theta_i(x)\}_{i=1}^N$ that is approximately localized at discrete spatial points $\{x_i\}$ [3]. The key property of the DVR basis functions is that they satisfy an approximate delta-function localization,

$$\theta_j(x_i) \approx \frac{\delta_{ij}}{\sqrt{\Delta x}}, \tag{S17}$$

which implies that evaluating a function at the grid points corresponds to projection onto the grid basis. Within this finite-dimensional subspace, the projection operator is

$$P_N = \sum_{i=1}^{N} |\theta_i\rangle\langle\theta_i|, \tag{S18}$$

and approaches completeness as the number of grid points N increases. An important advantage of the DVR is that the potential energy operator, being local in position, becomes diagonal in the grid basis to a very good approximation:

$$\langle\theta_i|V(\hat{x})|\theta_j\rangle \approx V(x_i)\,\delta_{ij}. \tag{S19}$$

This simplification arises because the basis functions are strongly localized near the grid points, and the integral for the matrix elements can be accurately approximated by a discrete quadrature using these points and corresponding weights. Consequently, the potential energy matrix V_{DVR} is constructed as a diagonal matrix whose entries are simply the values of the potential function evaluated at the grid points:

$$V_{ij}^{\mathrm{DVR}} = V(x_i)\,\delta_{ij}. \tag{S20}$$

By contrast, the kinetic energy operator involves derivatives and is nonlocal. Its matrix elements in the DVR basis are obtained by transforming the kinetic operator, which is diagonal in the primitive basis, into the grid basis via the orthogonal transformation. For a uniform grid on a finite interval, this transformation can be performed exactly and leads to an analytic expression for the kinetic energy matrix elements [4]:

$$T_{ij}^{\mathrm{DVR}} = \frac{\hbar^2}{2m\,\Delta x^2} \begin{cases} \dfrac{\pi^2}{3}, & i = j, \\ \dfrac{2(-1)^{i-j}}{(i-j)^2}, & i \neq j. \end{cases} \tag{S21}$$

This expression shows that the kinetic energy operator is represented by a full matrix with off-diagonal elements decaying as the inverse square of the distance between grid points. This nonlocal structure is essential to the spectral accuracy of the DVR method for smooth wavefunctions, distinguishing it from finite-difference approximations that typically yield sparse banded matrices.

III. MODEL AND PARAMETERS

A. Stacking

For the base monomer, we focus on the adenine molecule in our modeling [5]. Other nucleobases can be incorporated by adjusting the relevant parameters accordingly. The model Hamiltonian includes three excitonic states: the ground state $|g\rangle$, the bright excited state $|i\rangle$, and the dark excited state $|i'\rangle$. The bright and dark states are coupled via a conical intersection, while the ground state is also connected to the dark state through a second conical intersection. The Hamiltonian can be expressed in the following form:

$$\begin{aligned} H = {} & \varepsilon_i\,|i\rangle\langle i| + \varepsilon_{i'}\,|i'\rangle\langle i'| \\ & + M_2\Omega_2^2 Q_2 D_2\,(d_e\,|i\rangle\langle i| + d_d\,|i'\rangle\langle i'|) \\ & + M_1\Omega_1^2 Q_1 D_1\,(d_v\,|g\rangle\langle i'| + \text{h.c.}) \\ & + M_{1'}\Omega_{1'}^2 Q_{1'} D_{1'}\,(d_{v'}\,|i'\rangle\langle i| + \text{h.c.}) \end{aligned} \tag{S22}$$

where ε are the site energies of the excited states, M_i, D_i, and Ω_i are the masses, characteristic length scales, and frequencies of the modes with coordinates Q_i and d_i are the corresponding dimensionless displacements.

In our model, three spectral densities correspond to three correlation functions: one for the tuning mode and one for each of the two coupling modes. The dark state is coupled to the ground state via one conical intersection and the bright state is coupled to the dark state via another conical intersection. We can split Eq. (S22) into two parts [6]: $H = H_{mon} + H_{env}$. The monomer Hamiltonian is $H_{mon} = H_g + H_i + H_{i'}$, with $H_g = h_g \left|g\right\rangle \left\langle g\right|$, $H_i = (h_e + \varepsilon_i) \left|i\right\rangle \left\langle i\right|$ and $H_{i'} = (h_d + \varepsilon_{i'}) \left|i'\right\rangle \left\langle i'\right|$. The vibrational Hamiltonians h_2, h_1 and $h_{1'}$ are associated with the ground, bright and dark states, respectively. They are given by

$$h_0 = \frac{1}{2}\Big[\Omega_2\big(P_2^2 + Q_2^2\big) + \Omega_1\big(P_1^2 + Q_1^2\big) + \Omega_{1'}\big(P_{1'}^2 + Q_{1'}^2\big)\Big]. \tag{S23}$$

The vibrational Hamiltonian for the i-th ($i = 2, 1, 1'$) electronic state can be rewritten as $h_i = h_g + \Delta_i + s_i\kappa_t Q_2$ Here, Δ_i denotes the electronic reference energy of excited state. The dimensionless coefficient s_i specifies the relative displacement of the potential energy surface of state along the tuning coordinate Q_2. The parameter κ_t defines the linear coupling strength between the tuning mode and the electronic states, which determines the degree of potential energy displacement along Q_2. We assume $s_1 = 0$ $s_2 = +1$, and $s_3 = -1$, then

$$h_g = h_0 + \Delta_2, \tag{S24}$$

$$h_e = h_0 + \Delta_1 + \kappa_t Q_2, \tag{S25}$$

$$h_d = h_0 + \Delta_{1'} - \kappa_t Q_2, \tag{S26}$$

The electronic coupling between the two potential energy surface is assumed to linearly depend on $Q_{1,1'}$, such that $V = \Lambda Q_{1,1'}$, with the electronic coupling strength Λ.

In order to account for vibrational relaxation and environmental fluctuations, each primary vibrational mode is coupled to its own independent harmonic bath. Following the standard system-bath partitioning, this representation enables the environmental influence to be fully characterized by mode-specific spectral densities $J_a(\omega)$ and their corresponding bath orrelation functions. This mapping transforms the explicit-mode description into a system-bath form, where the bath degrees of freedom are represented by a set of harmonic oscillators $\{x_\alpha, p_\alpha, m_\alpha, \omega_\alpha\}$ and the system-bath coupling is linear in the system coordinates. The resulting system-bath Hamiltonian reads

$$H_{sb} = \sum_\alpha \left\{ \frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}m_\alpha\omega_\alpha^2 \left(x_\alpha - \frac{g_{2\alpha}}{m_\alpha\omega_\alpha^2}Q_2\right)^2 + \frac{1}{2}m_\alpha\omega_\alpha^2 \left(x_\alpha - \frac{g_{1\alpha}}{m_\alpha\omega_\alpha^2}Q_1\right)^2 + \frac{1}{2}m_\alpha\omega_\alpha^2 \left(x_\alpha - \frac{g_{1'\alpha}}{m_\alpha\omega_\alpha^2}Q_{1'}\right)^2 \right\}. \tag{S27}$$

Now we start from the generic shifted-bath-coordinate Hamiltonian expressed in terms of the system coordinates Q_i:

$$H \;=\; H_S(\{Q_i\}) + \sum_\alpha \left[\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}m_\alpha\omega_\alpha^2 \left(x_\alpha - \sum_{i\in\{2,1,1'\}} \frac{g_{i\alpha}}{m_\alpha\omega_\alpha^2}\, Q_i \right)^2 \right], \tag{S28}$$

where $H_S(\{Q_i\})$ is the bare system Hamiltonian in terms of Q_i, and the bath displacement depends linearly on these coordinates.

Expanding the square in Eq. (S28) leads to the standard linear-coupling representation with an explicit system-only renormalization term:

$$H = H_S(\{Q_i\}) + \sum_\alpha \left[\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}m_\alpha\omega_\alpha^2 x_\alpha^2 \right] - \sum_{i,\alpha} g_{i\alpha}\, x_\alpha Q_i + \frac{1}{2}\sum_{i,j}\left(\sum_\alpha \frac{g_{i\alpha}g_{j\alpha}}{m_\alpha\omega_\alpha^2} \right) Q_iQ_j. \tag{S29}$$

The third term on the right-hand side is the linear system-bath coupling and the last term is a system-only quadratic term that originates from the square of the shift; it acts as a renormalization of the bare system Hamiltonian.

Introduce shifted bath coordinates:

$$x_\alpha = x'_\alpha + \sum_{i=1}^{N} \frac{g_{i\alpha}}{m_\alpha\omega_\alpha^2}\, Q_i \qquad \Longleftrightarrow \qquad x'_\alpha = x_\alpha - \sum_i \frac{g_{i\alpha}}{m_\alpha\omega_\alpha^2}\, Q_i. \tag{S30}$$

Substituting Eq. (S30) into the expanded form (S29) and collecting terms yields (for each α)

$$\begin{aligned} H = H_S(\{Q_i\}) + \sum_\alpha \left[\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}m_\alpha\omega_\alpha^2 x'^2_\alpha \right] - \sum_{i,\alpha} g_{i\alpha}\, x'_\alpha Q_i \\ - \sum_{i,j,\alpha} \frac{g_{i\alpha}g_{j\alpha}}{m_\alpha\omega_\alpha^2}\, Q_iQ_j + \frac{1}{2}\sum_{i,j,\alpha} \frac{g_{i\alpha}g_{j\alpha}}{m_\alpha\omega_\alpha^2}\, Q_iQ_j. \end{aligned} \tag{S31}$$

Observe that the last two lines combine: the two system-only terms arising from the shift cancel partially, leaving a single renormalization term with a conventional prefactor. After simplifying we may absorb the resulting system-only term into a renormalized system Hamiltonian, $H_S^{(\mathrm{ren})}(\{Q_i\})$,

$$H \;=\; H_S^{(\mathrm{ren})}(\{Q_i\}) - \sum_{i,\alpha} g_{i\alpha}\, x'_\alpha Q_i + \sum_\alpha \left[\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 x'^2_\alpha\right]. \tag{S32}$$

Eq. (S32) is the three-level generalization form: the bath appears in its canonical harmonic form in the primed coordinates, and the system-bath interaction is linear in the primed bath coordinates and in the system coordinates Q_i.

Collecting the system-only contributions resulting from the shift gives the renormalization term

$$\Delta H_S \;=\; \frac{1}{2}\sum_{i,j}\left(\sum_\alpha \frac{g_{i\alpha} g_{j\alpha}}{m_\alpha \omega_\alpha^2}\right) Q_i Q_j. \tag{S33}$$

Hence one may define

$$H_S^{(\mathrm{ren})}(\{Q_i\}) \;=\; H_S(\{Q_i\}) \;+\; \Delta H_S.$$

For the three-level manifold $\{|g\rangle, |i\rangle, |i'\rangle\}$ we take nthe system coordinates Q_k to have the following state-dependent forms:

$$Q_2 = d_e\,|i\rangle\langle i| + d_d\,|i'\rangle\langle i'|, \tag{S34}$$

$$Q_1 = d_v\,\big(|g\rangle\langle i'| + h.c.\big), \tag{S35}$$

$$Q_{1'} = d_{v'}\,\big(|i'\rangle\langle i| + h.c.\big), \tag{S36}$$

Applying a canonical transformation, the H_{sb} is equivalently rewritten as:

$$\begin{aligned} H_{sb} =& \left(d_e\,|i\rangle\,\langle i| + d_d\,|i'\rangle\,\langle i'|\right) \sum_\alpha g'_{2\alpha} x'_\alpha \\ &+ \left(d_v\,|g\rangle\,\langle i'| + \text{h.c.}\right) \sum_\alpha g'_{1\alpha} x'_\alpha \\ &+ \left(d_{v'}\,|i'\rangle\,\langle i| + \text{h.c.}\right) \sum_\alpha g'_{1'\alpha} x'_\alpha, \end{aligned} \tag{S37}$$

The Hamiltonian for base stacking is extended from the exciton model of an individual base. Assuming that the base multimer shares a common ground state and that the excited states are stacked, the Hamiltonian can be written as

$$H = \sum_{i=1}^{N} \left(\varepsilon_i\,|i\rangle\,\langle i| + \varepsilon_{i'}\,|i'\rangle\,\langle i'|\right) + H_{sb} + H_{\mathrm{coupling}} + H_b, \tag{S38}$$

where

$$H_{\mathrm{coupling}} = \sum_{i=1}^{N} (\Delta\,|i\rangle\,\langle i+1| + h.c.), \tag{S39}$$

$$H_b = \sum_{i=1}^{N}\sum_{\alpha}^{\infty} \hbar\omega_{\alpha,i}(a^\dagger_{\alpha,i} a_{\alpha,i} + \frac{1}{2}), \tag{S40}$$

and

$$\begin{aligned} H_{sb} = -\sum_{i,i'}^{N} \Bigg[& \left(d_e\,|i\rangle\,\langle i| + d_d\,|i'\rangle\,\langle i'|\right) \sum_\alpha g'_{2\alpha,i} x'_{\alpha,i} \\ &+ \left(d_v\,|g\rangle\,\langle i'| + \text{h.c.}\right) \sum_\alpha g'_{1\alpha,i} x'_{\alpha,i} \\ &+ \left(d_{v'}\,|i'\rangle\,\langle i| + \text{h.c.}\right) \sum_\alpha g'_{1'\alpha,i} x'_{\alpha,i} \Bigg], \end{aligned} \tag{S41}$$

The symbol N represents the total number of stacked bases and Δ is the stacking strength between each bright state. The stacked adenine molecules are assumed to have identical excited-state energies. We adopted the Debye spectral density with a Lorentzian cutoff, given by the expression

$$J(\omega) = 2\lambda\omega_c \frac{\omega}{\omega^2 + \omega_c^2} \tag{S42}$$

where the cutoff frequency ω_c is 1000 cm^{-1}, and the reorganization energies λ are 833.5 cm^{-1}, 16.5 cm^{-1} and 33.5 cm^{-1}, respectively. Due to computational resource limitations, the full set of $3N$ thermal baths is reduced to three effective baths in practical calculations. The simplified form can be written as:

$$V_2 = \sum_{i,i'}^{N} \left(d_e \left|i\right\rangle \left\langle i\right| + d_d \left|i'\right\rangle \left\langle i'\right|\right) \sum_{\alpha} g'_{2\alpha} x'_{\alpha}, \tag{S43}$$

$$V_1 = \sum_{i'}^{N} \left(d_v \left|g\right\rangle \left\langle i'\right| + h.c.\right) \sum_{\alpha} g'_{1\alpha} x'_{\alpha}, \tag{S44}$$

$$V_{1'} = \sum_{i,i'}^{N} \left(d_{v'} \left|i'\right\rangle \left\langle i\right| + h.c.\right) \sum_{\alpha} g'_{1'\alpha} x'_{\alpha}. \tag{S45}$$

The parameters involved in the calculation are defined as: ε_i = 5 eV = 40325 cm^{-1}, $\varepsilon_{i'}$ = 3.5 eV = 28228 cm^{-1}, d_e = -0.8, d_d = 1, d_v = 1, $d_{v'}$ = 1, Δ = 200 cm^{-1}. Based on the constructed model with parameters, we calculated the population dynamics of thymine, guanine and cytosine molecules. The resulted data are shown in Fig. S1, Fig. S2 and Fig. S3, respectively. We have observed that the population deactivation from electronic bright state to the ground state can be significantly reduced during increasing numbers of nucleobases. More interestingly, we also calculated the population dynamics of stacking of nucleobases with natural order. We show the calculated results in Fig. S4. We observed that the decaying population from electronic bright to the ground state still can be strongly reduced due to the stacking effect.

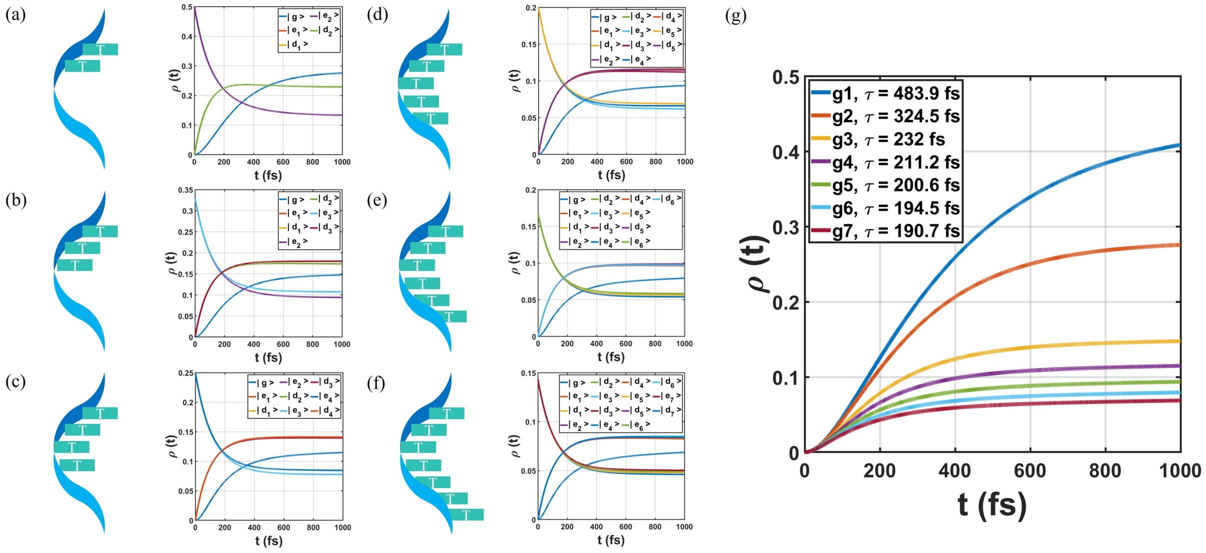

FIG. S1. Population dynamics of thymine molecules with the parameters ε_i = 4.8 eV = 38712 cm^{-1}, $\varepsilon_{i'}$ = 3.5 eV =28228 cm^{-1}, d_e = -0.8, d_d = 1, d_v = 1, $d_{v'}$ = 1, Δ = 170 cm^{-1}

B. Pairing

Under the influence of PCET mechanism, the Hamiltonian can be written in this form [7]

$$H = \varepsilon_{i'} \left|i'_A\right\rangle \left\langle i'_A\right| + \varepsilon_{i'} \left|i'_T\right\rangle \left\langle i'_T\right| + H_i \left|i_A\right\rangle \left\langle i_A\right| + H_i \left|i_T\right\rangle \left\langle i_T\right| + \Delta(\left|i_A\right\rangle \left\langle i_T\right| + h.c) + H_b + H_{sb}. \tag{S46}$$

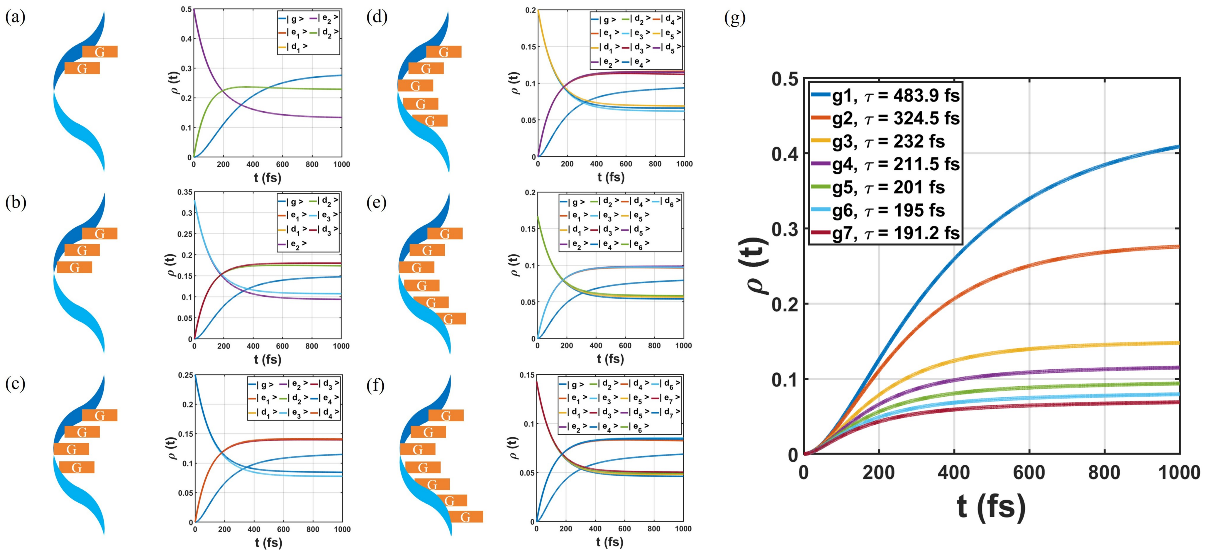

FIG. S2. Population dynamics of guanine molecules with the parameters ε_i = 4.8 eV = 38712 cm^{-1}, $\varepsilon_{i'}$ = 3.5 eV = 28228 cm^{-1}, d_e = -0.8, d_d = 1, d_v = 1, $d_{v'}$ = 1, Δ = 210 cm^{-1}

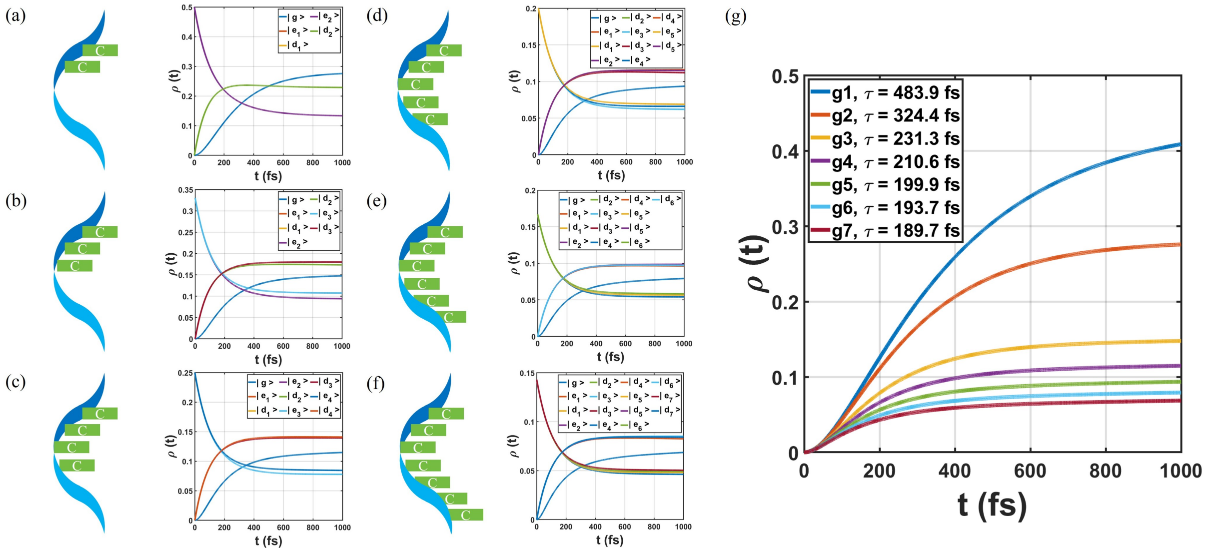

FIG. S3. Population dynamics of cytosine molecules with the parameters ε_i = 4.8 eV = 38712 cm^{-1}, $\varepsilon_{i'}$ = 3.5 eV = 28228 cm^{-1}, d_e = -0.8, d_d = 1, d_v = 1, $d_{v'}$ = 1, Δ = 120 cm^{-1}

The thermal bath Hamiltonian $\hat{H}_b$ is modeled as an ensemble of harmonic oscillators, which shows

$$H_b = \sum_{j=1}^{3}\sum_{\alpha}^{\infty} \hbar\omega_{\alpha,j}(a^{\dagger}_{\alpha,j}a_{\alpha,j} + \frac{1}{2}). \tag{S47}$$

For the dark state, the energy of H_i is fixed at $\varepsilon_{i'}$. The electronic-state Hamiltonian admits the expansion

$$H_i(\hat{x}, Q) = \frac{p_x^2}{2m_x} + \frac{p_Q^2}{2m_Q} + U_i(\hat{x}, Q) + \delta_i, \tag{S48}$$

where Q is the distance between the donor and acceptor and x is the distance between the proton and the donor-acceptor center. δ_i represents the energy offset between the two states.

In DVR, we employ $N_x = 100$ grid points to represent the proton coordinate x. The kinetic energy operator T_x and the potential energy surfaces $U_i(\hat{x}, Q)$ for each bright state are constructed accordingly. The potential $U_i(\hat{x}, Q)$

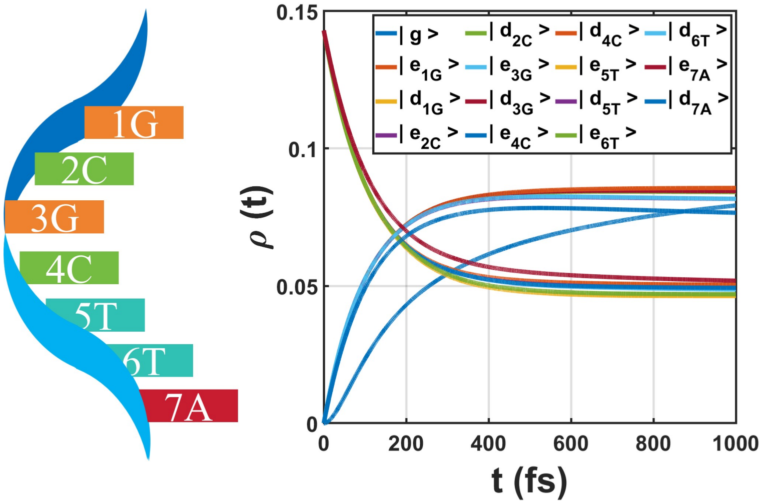

FIG. S4. Population dynamics of natural chain with the parameters ε_{iA} = 5 eV = 40325 cm^{-1}, $\varepsilon_{iG} = \varepsilon_{iC} = \varepsilon_{iT}$ = 4.8 eV = 38712 cm^{-1}, $\varepsilon_{i'}$ = 3.5 eV = 28228 cm^{-1}, d_e = -0.8, d_d = 1, d_v = 1, $d_{v'}$ = 1, Δ_{1G2C} = 104 cm^{-1}, Δ_{2C3G} = 73 cm^{-1}, Δ_{3G4C} = 122 cm^{-1}, Δ_{4C5T} = 91 cm^{-1}, Δ_{5T6T} = 220 cm^{-1}, Δ_{6T7A} = 3 cm^{-1}

consists of a double Morse potential [8], which is given by

$$U_i(\hat{x}, Q) = D_i^l \left[1 - e^{-\alpha(x+Q/2-x_0)}\right]^2 + D_i^r \left[1 - e^{-\alpha(Q/2-x-x_0)}\right]^2, \tag{S49}$$

where Q is the fixed donor-acceptor distance, x_0 defines the position of the potential minima. For each bright state, the Hamiltonian $H_i = T_x + U_i(x, Q)$ is diagonalized in the DVR basis, and the lowest $N_b = 12$ eigenstates are selected to construct a reduced vibronic basis. Consistent with the setup described in part A of section III, the simplified H_{sb} term is defined as follows,

$$V_2 = \sum_{i,i'}^{N} \left(d_e \left|i\right\rangle \left\langle i\right| + d_d \left|i'\right\rangle \left\langle i'\right|\right) \sum_{\alpha} g'_{2\alpha} x'_{\alpha}, \tag{S50}$$

$$V_1 = \sum_{i,i'}^{N} \left(d_v \left|g\right\rangle \left\langle i'\right| + h.c.\right) \sum_{\alpha} g'_{1\alpha} x'_{\alpha}, \tag{S51}$$

$$V_{1'} = \sum_{i,i'}^{N} \left(d_{v'} \left|i'\right\rangle \left\langle i\right| + h.c.\right) \sum_{\alpha} g'_{1'\alpha} x'_{\alpha}. \tag{S52}$$

In the A–T base pair, adenine is designated as the donor molecule and thymine as the acceptor. The dark-state energies $\varepsilon_{i'}$ of both molecules are set to 28000 cm^{-1}. The coupling strength Δ between the two bright states is set to 190 cm^{-1} and the energy offset δ_i is set to 2500 cm^{-1}. Regarding the double Morse potential, the curvature parameter is defined as $\alpha = 2$ Å^{-1}. The well depths are specified as follows: D_A^l = 43000 cm^{-1}, D_A^r = 39000 cm^{-1}, D_T^l = 39000 cm^{-1}, and D_T^r = 34000 cm^{-1}.

For the C–G base pair, the calculations can be finished by following the same procedure. The parameters used in the calculations are as follows: $Q = 3$ Å, $x_0 = 1$ Å, $\alpha = 2$ Å^{-1}, δ_i = 2500 cm^{-1}, Δ = 90 cm^{-1}, D_G^l = 39000 cm^{-1}, D_G^r = 34000 cm^{-1}, D_C^l = 39000 cm^{-1}, and D_C^r = 34000 cm^{-1}.

IV. CURVE FITTING

This section describes the curve fitting method employed in this work. The lifetime data were analyzed using the Curve Fitting tool in MATLAB R2019a. By selecting an appropriate fitting function

$$y = Ae^{-\frac{t}{\tau}} + b, \tag{S53}$$

nonlinear fitting was performed on the time-resolved data to extract the corresponding lifetime parameter τ.

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