

Supplementary Information

**Dynamical disorder and Resonance Energy
Transfer: a novel quantum-classical approach**

Francesco Di Maiolo^{*,†,‡} and Anna Painelli^{*,†}

*†Department of Chemistry, Life Science and Environmental Sustainability, Università di
Parma, 43124 Parma, Italy*

*‡Present address: Institute of Physical and Theoretical Chemistry, Goethe University,
Frankfurt, Max-von-Laue-Str. 7, 60438 Frankfurt, Germany*

E-mail: DiMaiolo@chemie.uni-frankfurt.de; anna.painelli@unipr.it

1 Computational details

To calculate the non-adiabatic eigenstates of \hat{H}^{mol} in Eq.1 (main text), we diagonalize the Hamiltonian matrix written on the direct-product basis $(|N\rangle, |Z\rangle) \otimes (|0\rangle, |1\rangle, \dots, |m\rangle)$, where $|v\rangle$ are the eigenstates of the harmonic oscillator in the last term of Eq.1 (main text) and m is large enough to ensure convergence of calculated properties. Results in Figures 2 and 3 (main text) are obtained truncating the vibrational space to $m = 12$, thus leading to an \mathcal{S} space of dimension 26. F_{or} is defined on a 80 points grid, with spacing 0.022 eV and F_{or} derivatives are calculated as finite differences, setting the step size equal to the solvent grid spacing. Equation 2 is integrated using the Short-Iterative-Arnoldi (SIA) algorithm with a time step 1.5 fs in Fig.2 (main text) and 0.05 fs in Figure 3 (main text).^{1,2} Actually, Eq.3 (main text) does not properly describe the relaxation towards equilibrium. We trace this problem to the $\mathcal{S}\text{-}\mathcal{B}_2$ interaction terms (third and fourth terms in Eq. 3, main text) that, even close to the equilibrium, lead to a spurious mixing among states belonging to the ground and excited state electronic manifolds. To fix this problem we force these mixing terms to vanish at the equilibrium, substituting in Eq. 3 (main text):

$$\rho_{ab} \rightarrow \rho_{ab} \left[1 - \int dF_{or} \sigma_{11}(F_{or}; t) \right], \quad \forall a \neq b, \quad (1)$$

where $\sigma_{11}(F_{or}; t)$ is the F_{or} -dependent ground state population. Results in Figs.2 and 3 (main text) are obtained in this approximation.

\hat{H}^{RET} is written on the Hilbert space spanned by $(|N_{\mathcal{D}}N_{\mathcal{A}}\rangle, |N_{\mathcal{D}}Z_{\mathcal{A}}\rangle, |Z_{\mathcal{D}}N_{\mathcal{A}}\rangle, |Z_{\mathcal{D}}Z_{\mathcal{A}}\rangle) \otimes (|0\rangle_{\mathcal{D}}, \dots, |n\rangle_{\mathcal{D}}, \dots) \otimes (|0\rangle_{\mathcal{A}}, \dots, |m\rangle_{\mathcal{A}}, \dots)$, where we truncate the harmonic oscillator basis imposing that $n + m < \beta$, with β large enough to reach convergence on calculated properties. In Figures 4 and 5 (main text), we set $\beta = 13$, for a grandtotal of $N = 364$ basis states. Due to the large dimension of the RET-pair basis, we only account for $R_{ab,cd}$ terms in the Redfield tensor relevant to states with $|\omega_{ab} - \omega_{cd}| \leq \alpha$, with $\alpha = 0.02$ eV.^{3,4} Larger α values slow down the calculation without affecting the results. For the RET-pair, the hybrid density

operator is defined on a grid of 23×23 points, with step $\Delta F_D^{or} = 0.046$ eV and $\Delta F_A^{or} = 0.056$ eV. Finite-difference expressions for the derivatives are calculated using the same steps. The SIA algorithm (time step 1.5 fs) is used to integrate the differential equations. To speed up the calculations without compromising the accuracy of the results, states higher in energy than the initial coherent state are neglected.

The global \mathcal{A}^* population operator is defined measuring the weight of the \mathcal{A}^* state:⁵ $\hat{P}_{\mathcal{A}^*} = |\mathcal{A}^*\rangle\langle\mathcal{A}^*|$,^{6,7} where $|\mathcal{A}^*\rangle = -\sqrt{\rho_A}|N_A\rangle + \sqrt{1-\rho_A}|Z_A\rangle$, with $\rho_A = 0.5 \cdot (1 - z_A / \sqrt{z_A^2 + \tau_A^2})$.

2 Adiabatic system-solvent Hamiltonian and steady-state optical spectra

The Hamiltonian for a polar molecule in a polar solvent reads:

$$\hat{H}(F_{or}) = \hat{H}^{mol} - F_{or}\hat{\rho} + \frac{F_{or}^2}{4\epsilon_{or}}, \quad (2)$$

where all quantities are defined in the main text. The above Hamiltonian describes a molecule in terms of coupled electronic and vibrational states, fully accounting for the non-adiabatic nature of the electron-vibration coupling. The F_{or} -dependent Hamiltonian in equation (2) is diagonalized, for different F_{or} values, on the non-adiabatic electron-vibration basis (as defined in the main text), to get F_{or} -dependent vibronic eigenstates $|\psi_a(F_{or})\rangle$ and energy $E_k(F_{or})$. These energies define relevant potential energy curves. F_{or} -dependent spectra can be calculated from the transition dipole moments $\mu_{ab}(F_{or}) = \langle\psi_a(F_{or})|\hat{\mu}|\psi_b(F_{or})\rangle$ and frequencies $\omega_{ab}(F_{or}) = (E_a(F_{or}) - E_b(F_{or}))/\hbar$, assigning a Gaussian lineshape to each vibronic line, with standard deviation σ .

To account for thermal disorder and the resulting inhomogeneous broadening, spectra are calculated as ensemble averages, summing over the spectra calculated at different F_{or} values, weighted for the relevant Boltzmann distribution. In particular, for absorption spectra we

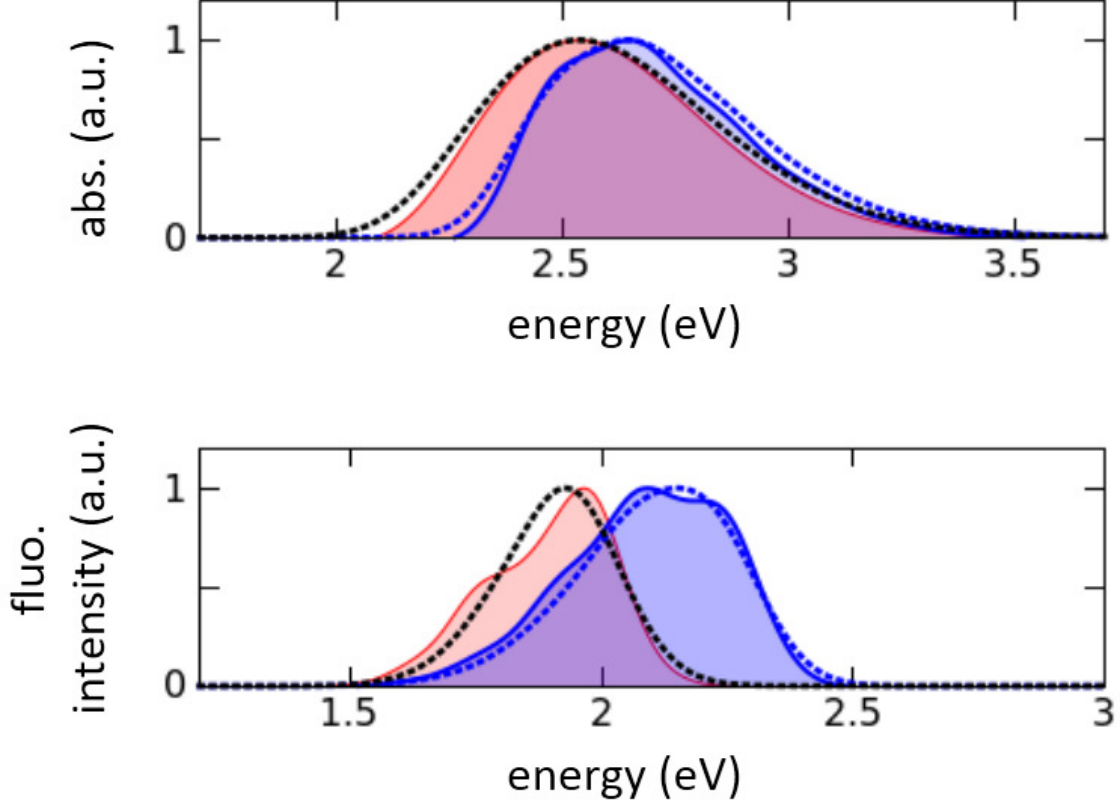


Figure 1: DCM spectra calculated in CHCl_3 and DMSO. Top panel compares absorption spectra calculated in the main text (Fig.3d) with those calculated upon thermal averaging on the ground state distribution (dotted blue and black lines refer to CHCl_3 and DMSO, respectively). Bottom panel compares long-time fluorescence spectra calculated in the main text (Fig.3j) with steady-state fluorescence spectra calculated upon thermal averaging on the fluorescent state distribution. All model parameters are the same as in the main text; in Eqs.3 and 4 we set $\sigma = 0.06$ eV.

account for the Boltzmann distribution associated with the lowest vibronic eigenstate (the ground state) $E_1(F_{or})$, while for emission spectra we consider the energy of the fluorescent state, $E_f(F_{or})$. The explicit expression for the absorption spectrum is:⁹

$$A(\omega) \propto \omega \sum_{F_{or}} \exp\left[\frac{-E_1(F_{or})}{k_b T}\right] \sum_a |\mu_{a1}(F_{or})|^2 \exp\left[-\frac{(\hbar\omega_{a1}(F_{or}) - \hbar\omega)^2}{2\sigma^2}\right], \quad (3)$$

where the first sum runs over different solvent configurations, F_{or} , while the second sum runs over all the excited F_{or} -dependent eigenstates of the dye.

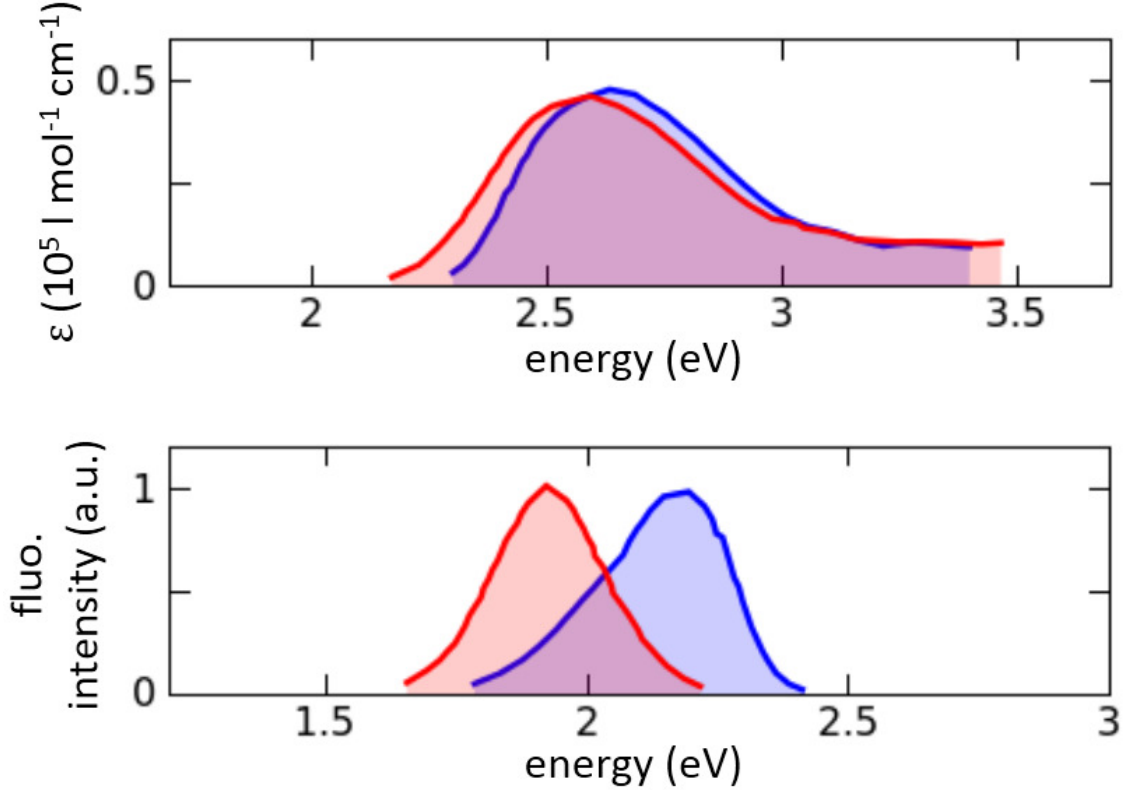


Figure 2: DCM experimental absorption (top panel) and fluorescence (bottom panel) spectra collected in CHCl_3 (blue) and DMSO (red). Data adapted from Ref.⁸

Similarly, steady-state fluorescence spectrum is calculated as:⁹

$$F(\omega) \propto \omega^3 \sum_{F_{or}} \exp \left[\frac{-E_f(F_{or})}{k_b T} \right] \sum_a |\mu_{af}(F_{or})|^2 \exp \left[-\frac{(\hbar\omega_{af}(F_{or}) - \hbar\omega)^2}{2\sigma^2} \right], \quad (4)$$

where the second sum runs over all the system eigenstates lower in energy than the fluorescent state, $|\psi_f(F_{or})\rangle$. The fluorescent state is singled out by looking at the transition dipole moments from the ground state, since the fluorescent state will be the first excited state with a large $|\langle \psi_f(F_{or}) | \hat{\mu} | \psi_1(F_{or}) \rangle|$.

Fig.1 compares absorption and steady-state (long t' behavior) fluorescence spectra calculated for DCM in CHCl_3 and DMSO according to equations (3) and (4), setting $\sigma = 0.06$ eV, with spectra obtained from the Fourier transform of the relevant dipole-dipole correlation functions, as discussed in the main text. The agreement is very good, a result that con-

firm the reliability of the dynamical behavior calculated using the Redfield-Smoluchowsky approach. Specifically, we observe that minor differences in bandshapes are expected: in the steady state calculation, a Gaussian bandshape is imposed to each vibronic line with an *ad hoc* choice of σ . On the contrary bandshapes come out naturally from the Redfield-Smoluchowsky dynamics, without any *ad hoc* hypothesis on bandshapes and bandwidths.

3 Redfield tensor

The expression for the element of the Redfield tensor $R_{ab,cd}$ (Eq.3, main text) reads:¹

$$R_{ab,cd} = -\delta_{b,d} \sum_e \Theta_{ae,ec}^+ - \delta_{a,c} \sum_e \Theta_{de,eb}^- + \Theta_{db,ac}^+ + \Theta_{db,ac}^- \quad (5)$$

where the pedices run on the eigenstates of the relevant system, either \hat{H}^{mol} or \hat{H}^{RET} , $\delta_{b,d}$ and $\delta_{a,c}$ are Kronecker delta, and $\Theta_{db,ac}^{+(-)}$ is the generic element of the kinetic coefficient tensor, $\Theta^{+(-)}$.

When the system \mathcal{S} is defined by a single dye, the elements of $\Theta^{+(-)}$ are:³

$$\Theta_{db,ac}^+ = \gamma \left(d_{db} d_{ac}^\dagger \langle \hat{n}(\omega_{ac}) \rangle_b + d_{db}^\dagger d_{ac} \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \right), \quad (6)$$

$$\Theta_{db,ac}^- = \gamma \left(d_{db} d_{ac}^\dagger \langle \hat{n}(\omega_{bd}) \rangle_b + d_{db}^\dagger d_{ac} \langle \hat{n}(\omega_{db}) + 1 \rangle_b \right), \quad (7)$$

where $d_{ac}^{(\dagger)} = \langle \psi_a | \hat{d}^{(\dagger)} | \psi_c \rangle$ is the matrix element of the creation (annihilation) operator associated with the molecular vibration, and $\langle \hat{n}(\omega_{ac}) \rangle_b = (\exp[\hbar\omega_{ac}/k_b T] - 1)^{-1}$ is the Bose-Einstein distribution relevant to the Redfield bath, \mathcal{B}_1 . As discussed in the main text, γ measures the \mathcal{SB}_1 coupling strength.

When the system \mathcal{S} describes a RET-pair, the elements of the kinetic coefficient tensors

read:³

$$\begin{aligned}
\Theta_{db,ac}^+ = & \gamma \left[d_{db} d_{ac}^\dagger \langle \hat{n}(\omega_{ac}) \rangle_b + d_{db}^\dagger d_{ac} \langle \hat{n}(\omega_{ca}) + 1 \rangle_b + a_{db} a_{ac}^\dagger \langle \hat{n}(\omega_{ac}) \rangle_b \right. \\
& + a_{db}^\dagger a_{ac} \langle \hat{n}(\omega_{ca}) + 1 \rangle_b + d_{db} a_{ac}^\dagger \langle \hat{n}(\omega_{ac}) \rangle_b + d_{db}^\dagger a_{ac} \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\
& \left. + a_{db} d_{ac}^\dagger \langle \hat{n}(\omega_{ac}) \rangle_b + a_{db}^\dagger d_{ac} \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \right] \quad (8)
\end{aligned}$$

and

$$\begin{aligned}
\Theta_{db,ac}^- = & \gamma \left[d_{db} d_{ac}^\dagger \langle \hat{n}(\omega_{bd}) \rangle_b + d_{db}^\dagger d_{ac} \langle \hat{n}(\omega_{db}) + 1 \rangle_b + a_{db} a_{ac}^\dagger \langle \hat{n}(\omega_{bd}) \rangle_b \right. \\
& + a_{db}^\dagger a_{ac} \langle \hat{n}(\omega_{db}) + 1 \rangle_b + d_{db} a_{ac}^\dagger \langle \hat{n}(\omega_{bd}) \rangle_b + d_{db}^\dagger a_{ac} \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\
& \left. + a_{db} d_{ac}^\dagger \langle \hat{n}(\omega_{bd}) \rangle_b + a_{db}^\dagger d_{ac} \langle \hat{n}(\omega_{db}) + 1 \rangle_b \right], \quad (9)
\end{aligned}$$

where $\hat{d}^{(\dagger)}$ and $\hat{a}^{(\dagger)}$ are the boson creation (annihilation) operators associated with the vibrational coordinate on \mathcal{D} and \mathcal{A} , respectively.

4 Derivation of Eq. 3, main text

We consider the simplest case where \mathcal{S} corresponds to a single molecule. The orientational component of the solvent reaction field can be treated as an effective harmonic mode,¹⁰ the relevant Hamiltonian being:

$$\hat{H}_{\mathcal{B}_2} = \frac{\hbar\omega_{or}}{2} (\hat{f}_{or}^2 + \hat{p}_{or}^2), \quad (10)$$

where ω_{or} is the frequency of the polar solvation mode, and \hat{f}_{or} (\hat{p}_{or}) is the relevant coordinate (momentum) operator. In the overdamped limit (see below) the frequency ω_{or} becomes irrelevant and disappears from the equations. The interaction between the molecule and the

polar solvent is:

$$\hat{H}_{\mathcal{SB}_2} = -\sqrt{\hbar\omega_{or}2\varepsilon_{or}}\hat{f}_{or}\hat{\rho}, \quad (11)$$

where ε_{or} is the solvent orientational relaxation energy and $\hat{\rho}$ is the system ionicity operator (proportional to the molecule dipole moment operator), defined in the main text.

We perform a partial Wigner transformation with respect to the solvent degrees of freedom^{11,12} and rewrite Eqs.10 and 11 as:

$$H_{\mathcal{B}_2}^w(f_{or}, p_{or}) = \frac{\hbar\omega_{or}}{2}(f_{or}^2 + p_{or}^2), \quad (12)$$

$$\hat{H}_{\mathcal{SB}_2}^w(f_{or}) = -\sqrt{\hbar\omega_{or}2\varepsilon_{or}}f_{or}\hat{\rho}, \quad (13)$$

where the w apex stands for partial Wigner transform. In other words, $\hat{H}_{\mathcal{B}_2}^w$ is transformed in a continuous function of f_{or} and p_{or} and $\hat{H}_{\mathcal{SB}_2}^w$ in a continuous function of f_{or} . The same transformation is applied to the density operator so that the matrix elements of the density operator, σ_{ab} , become functions of f_{or} and p_{or} .

We start at time $t = 0$ with disentangled \mathcal{S} - \mathcal{B}_2 states, so that the density operator is:

$$\hat{\sigma}^w(f_{or}, p_{or}; t = 0) = \hat{\sigma} \otimes w_{\mathcal{B}_2}(f_{or}, p_{or}), \quad (14)$$

where $w_{\mathcal{B}_2}(f_{or}, p_{or})$ is a continuous function of f_{or} and p_{or} representing the solvent initial distribution.

The generic element of the density matrix, $\sigma_{ab}^w = \sigma_{ab}^w(f_{or}, p_{or}; t)$, evolves in time according

to the following equation:^{13,14}

$$\begin{aligned}
\frac{\partial \sigma_{ab}^w}{\partial t} &= -i\omega_{ab}\sigma_{ab}^w + \sum_{c,d} R_{ab,cd}\sigma_{cd}^w \\
&+ \left\{ \frac{-\sqrt{\hbar\omega_{or}2\varepsilon_{or}}}{i\hbar} f_{or} \sum_c (\rho_{ac}\sigma_{cb}^w - \sigma_{ac}^w\rho_{cb}) \right. \\
&- \frac{\sqrt{\hbar\omega_{or}2\varepsilon_{or}}}{2\hbar} \sum_c \left(\rho_{ac} \frac{\partial \sigma_{cb}^w}{\partial p_{or}} + \frac{\partial \sigma_{ac}^w}{\partial p_{or}} \rho_{cb} \right) \\
&+ \omega_{or} \left(f_{or} \frac{\partial \sigma_{ab}^w}{\partial p_{or}} - p_{or} \frac{\partial \sigma_{ab}^w}{\partial f_{or}} \right) \\
&\left. + \zeta_{or} \frac{\partial}{\partial p_{or}} \left(p_{or}\sigma_{ab}^w + \frac{k_b T}{\hbar\omega_{or}} \frac{\partial \sigma_{ab}^w}{\partial p_{or}} \right) \right\}, \quad \forall a, b = 1, \dots, N, \tag{15}
\end{aligned}$$

where the first line of the right hand side (rhs) accounts for Liouvillian as well as Redfield dynamics. The second line describes the effect of the solvent on the system dynamics, whereas the third line accounts for the system-to-solvent feedback. The fourth and fifth lines describe the polar solvent dynamics as affected by the drift-diffusion Fokker-Planck term. ζ_{or} is the solvent friction coefficient, k_b is the Boltzmann constant and T is the temperature.

Since f_{or} is an overdamped coordinate (i.e. $\zeta_{or} \gg \omega_{or}$), the corresponding momentum p_{or} rapidly reaches equilibrium.¹⁵ Following Ref.¹⁶ we integrate p_{or} out of Eq.15 to get:

$$\begin{aligned}
\frac{\partial \sigma_{ab}^w}{\partial t} &= -i\omega_{ab}\sigma_{ab}^w + \sum_{c,d} R_{ab,cd}\sigma_{cd}^w \\
&- \frac{\sqrt{\hbar\omega_{or}2\varepsilon_{or}}}{i\hbar} f_{or} \sum_c (\rho_{ac}\sigma_{cb}^w - \sigma_{ac}^w\rho_{cb}) \\
&- \omega_{or} \frac{\partial}{\partial f_{or}} (\bar{p}_{or}\sigma_{ab}^w), \quad \forall a, b = 1, \dots, N, \tag{16}
\end{aligned}$$

where $\sigma_{ab}^w = \sigma_{ab}^w(f_{or}; t) = \int dp_{or} \sigma_{ab}^w(f_{or}, p_{or}; t)$ and in the bottom line we introduced $\bar{p}_{or}\sigma_{ab}^w(f_{or}; t) = \int dp_{or} p_{or}\sigma_{ab}^w(f_{or}, p_{or}; t)$. To obtain the momentum equation we multiply both members of

Eq.15 by p_{or} and integrate with respect to p_{or} , getting:

$$\begin{aligned}
\frac{\partial}{\partial t}(\sigma_{ab}^w \bar{p}_{or}) &= -i\omega_{ab} \sigma_{ab}^w \bar{p}_{or} + \sum_{c,d} R_{ab,cd} \sigma_{cd}^w \bar{p}_{or} \\
&\quad - \frac{\sqrt{\hbar\omega_{or}2\varepsilon_{or}}}{i\hbar} f_{or} \sum_c (\rho_{ac} \sigma_{cb}^w \bar{p}_{or} - \sigma_{ac}^w \bar{p}_{or} \rho_{cb}) \\
&\quad - \omega_{or} \left(f_{or} \sigma_{ab}^w + \frac{\partial}{\partial f_{or}} \sigma_{ab}^w \langle p_{or}^2 \rangle \right) \\
&\quad + \frac{\sqrt{\hbar\omega_{or}2\varepsilon_{or}}}{2\hbar} \sum_c (\rho_{ac} \sigma_{cb}^w + \sigma_{ac}^w \rho_{cb}) \\
&\quad - \zeta_{or} \sigma_{ab}^w \bar{p}_{or}, \quad \forall a, b = 1, \dots, N,
\end{aligned} \tag{17}$$

where we used the definition $\sigma_{ab}^w(f_{or}; t) \langle p_{or}^2 \rangle = \int dp_{or} p_{or}^2 \sigma_{ab}^w(f_{or}, p_{or}; t)$.

The f_{or} derivative of Eq.17 leads to:

$$\begin{aligned}
\frac{1}{\zeta_{or}} \frac{\partial^2}{\partial f_{or} \partial t} (\sigma_{ab}^w \bar{p}_{or}) &= -i\omega_{ab} \frac{1}{\zeta_{or}} \frac{\partial}{\partial f_{or}} \sigma_{ab}^w \bar{p}_{or} + \frac{1}{\zeta_{or}} \frac{\partial}{\partial f_{or}} \sum_{c,d} R_{ab,cd} \sigma_{cd}^w \bar{p}_{or} \\
&\quad - \frac{\sqrt{\hbar\omega_{or}2\varepsilon_{or}}}{i\hbar} \frac{1}{\zeta_{or}} \frac{\partial}{\partial f_{or}} \left[f_{or} \sum_c (\rho_{ac} \sigma_{cb}^w \bar{p}_{or} - \sigma_{ac}^w \bar{p}_{or} \rho_{cb}) \right] \\
&\quad - \omega_{or} \frac{1}{\zeta_{or}} \frac{\partial}{\partial f_{or}} \left(f_{or} \sigma_{ab}^w + \frac{\partial}{\partial f_{or}} \sigma_{ab}^w \langle p_{or}^2 \rangle \right) \\
&\quad + \frac{\sqrt{\hbar\omega_{or}2\varepsilon_{or}}}{2\hbar} \frac{1}{\zeta_{or}} \frac{\partial}{\partial f_{or}} \sum_c (\rho_{ac} \sigma_{cb}^w + \sigma_{ac}^w \rho_{cb}) \\
&\quad - \frac{\partial}{\partial f_{or}} (\sigma_{ab}^w \bar{p}_{or}), \quad \forall a, b = 1, \dots, N,
\end{aligned} \tag{18}$$

Exploiting Eq.16, we rewrite the last line on the right hand side of Eq.18 as:

$$\begin{aligned}
-\frac{\partial}{\partial f_{or}} (\sigma_{ab}^w \bar{p}_{or}) &= \frac{1}{\omega_{or}} \frac{\partial \sigma_{ab}^w}{\partial t} + \frac{1}{\omega_{or}} i\omega_{ab} \sigma_{ab}^w - \frac{1}{\omega_{or}} \sum_{c,d} R_{ab,cd} \sigma_{cd}^w \\
&\quad + \frac{\sqrt{\hbar\omega_{or}2\varepsilon_{or}}}{i\hbar} \frac{1}{\omega_{or}} f_{or} \sum_c (\rho_{ac} \sigma_{cb}^w - \sigma_{ac}^w \rho_{cb}), \quad \forall a, b = 1, \dots, N.
\end{aligned} \tag{19}$$

Combining Eq.19 with 18 and neglecting all terms proportional to \bar{p}_{or}/ζ_{or} (overdamped

limit), we get:

$$\begin{aligned}
\frac{\zeta_{or}}{\omega_{or}} \frac{\partial}{\partial t} \sigma_{ab}^w &= -\frac{\zeta_{or}}{\omega_{or}} i\omega_{ab} \sigma_{ab}^w + \frac{\zeta_{or}}{\omega_{or}} \sum_{c,d} R_{ab,cd} \sigma_{cd}^w \\
&\quad - \frac{\sqrt{\hbar\omega_{or}2\varepsilon_{or}}}{i\hbar} \frac{\zeta_{or}}{\omega_{or}} f_{or} \sum_c (\rho_{ac} \sigma_{cb}^w - \sigma_{ac}^w \rho_{cb}) \\
&\quad + \frac{\partial}{\partial f_{or}} \left\{ \frac{-\sqrt{\hbar\omega_{or}2\varepsilon_{or}}}{2\hbar} \sum_c (\rho_{ac} \sigma_{cb}^w + \sigma_{ac}^w \rho_{cb}) \right. \\
&\quad \left. + \omega_{or} f_{or} \sigma_{ab}^w + \omega_{or} \frac{\partial}{\partial f_{or}} \sigma_{ab}^w \frac{k_b T}{\hbar\omega_{or}} \right\}, \quad \forall a, b = 1, \dots, N,
\end{aligned} \tag{20}$$

where we used $\langle p_{or}^2 \rangle = k_b T / \hbar\omega_{or}$. Rescaling the total density operator as $\hat{\sigma}^w = \hat{\sigma}^w \zeta_{or} / \omega_{or}$, setting $F_{or} = \sqrt{\hbar\omega_{or}2\varepsilon_{or}} f_{or}$ and introducing the solvent longitudinal relaxation time $\tau_l = \zeta_{or} / \omega_{or}^2$,¹⁷ we finally get:

$$\begin{aligned}
\frac{\partial}{\partial t} \sigma_{ab}^w(F_{or}; t) &= -i\omega_{ab} \sigma_{ab}^w(F_{or}; t) + \sum_{c,d} R_{ab,cd} \sigma_{cd}^w(F_{or}; t) \\
&\quad + \frac{-F_{or}}{i\hbar} \sum_c (\rho_{ac} \sigma_{cb}^w(F_{or}; t) - \sigma_{ac}^w(F_{or}; t) \rho_{cb}) \\
&\quad - \frac{\varepsilon_{or}}{\tau_l} \sum_c \left(\rho_{ac} \frac{\partial \sigma_{cb}^w(F_{or}; t)}{\partial F_{or}} + \frac{\partial \sigma_{ac}^w(F_{or}; t)}{\partial F_{or}} \rho_{cb} \right) \\
&\quad + \frac{1}{\tau_l} \frac{\partial}{\partial F_{or}} \left(F_{or} \sigma_{ab}^w(F_{or}; t) + k_b T 2\varepsilon_{or} \frac{\partial}{\partial F_{or}} \sigma_{ab}^w(F_{or}; t) \right).
\end{aligned} \tag{21}$$

A well-known problem of coupled quantum-classical dynamics is due to the fourth term in Eq.21 that breaks the positivity of the density matrix.¹⁸⁻²⁰ A mean-field approximation to this term solves the problem:

$$-\frac{\varepsilon_{or}}{\tau_l} \sum_c \left(\rho_{ac} \frac{\partial \sigma_{cb}^w(F_{or}; t)}{\partial F_{or}} + \frac{\partial \sigma_{ac}^w(F_{or}; t)}{\partial F_{or}} \rho_{cb} \right) \simeq -\frac{2\varepsilon_{or}}{\tau_l} \langle \hat{\rho}(F_{or}; t) \rangle \frac{\partial \sigma_{ab}^w(F_{or}; t)}{\partial F_{or}}, \tag{22}$$

where $\langle \hat{\rho}(F_{or}; t) \rangle = Tr_S[\hat{\rho} \hat{\sigma}(F_{or}; t)]$. Plugging this approximation into Eq.21, we get Eq. 3 in the main text.

5 \mathcal{DA} energy gap

The Hamiltonian that describes the RET-pair in solution reads:

$$\hat{H}(F_{\mathcal{D}}^{or}, F_{\mathcal{A}}^{or}) = \hat{H}^{RET} - F_{\mathcal{D}}^{or} \hat{\rho}_{\mathcal{D}} - F_{\mathcal{A}}^{or} \hat{\rho}_{\mathcal{A}} + \frac{(F_{\mathcal{D}}^{or})^2}{4\epsilon_{\mathcal{D}}^{or}} + \frac{(F_{\mathcal{A}}^{or})^2}{4\epsilon_{\mathcal{A}}^{or}}, \quad (23)$$

where all variables and operators are defined in the main text. Diagonalizing the above Hamiltonian for different $(F_{\mathcal{D}}^{or}, F_{\mathcal{A}}^{or})$ values, we get the potential energy surfaces (PES) with respect to $F_{\mathcal{D}}^{or}, F_{\mathcal{A}}^{or}$, namely $E_k(F_{\mathcal{D}}^{or}, F_{\mathcal{A}}^{or})$, $\forall k = 1, \dots, N$, where N is \hat{H}^{RET} basis dimension. In Fig.5b in the main text, colored lines show solvent configurations where degeneracy is observed between the lowest state of the excited energy donor, $E_{\mathcal{D}^*,1}(F_{\mathcal{D}}^{or}, F_{\mathcal{A}}^{or})$, and each of the five lowest states of the excited energy acceptor, $E_{\mathcal{A}^*,i}(F_{\mathcal{D}}^{or}, F_{\mathcal{A}}^{or})$, $\forall i = 1, \dots, 5$. To single out $E_{\mathcal{D}^*,1}$ we look for the first eigenstate with $\langle \hat{\rho}_{\mathcal{D}} \rangle > 0.5$. Similarly, to find $E_{\mathcal{A}^*,i}$, $\forall i = 1, \dots, 5$, we look for the five lowest states having $\langle \hat{\rho}_{\mathcal{A}} \rangle > 0.5$.

6 Equation of motion for 2-dyes

Eq. 3 in the main text can be expanded to account for the interaction of the polar solvent with the two molecules in the RET-pair. Specifically, the energy donor (\mathcal{D}) and energy acceptor (\mathcal{A}) molecules feel two different orientational solvation fields, $F_{\mathcal{D}}^{or}$ and $F_{\mathcal{A}}^{or}$, respectively. The

dynamical equation for the RET-system interacting with \mathcal{B}_1 and \mathcal{B}_2 reads:

$$\begin{aligned}
\frac{\partial}{\partial t}\sigma_{ab} = & -i\omega_{ab}\sigma_{ab} + \sum_{c,d} R_{ab,cd}\sigma_{cd} \\
& + \frac{-F_{\mathcal{D}}^{or}}{i\hbar} \sum_c (\rho_{\mathcal{D}}^{ac}\sigma_{cb} - \sigma_{ac}\rho_{\mathcal{D}}^{cb}) - \frac{F_{\mathcal{A}}^{or}}{i\hbar} \sum_c (\rho_{\mathcal{A}}^{ac}\sigma_{cb} - \sigma_{ac}\rho_{\mathcal{A}}^{cb}) \\
& - \frac{\varepsilon_{\mathcal{D}}^{or}}{\tau_l} \sum_c \left(\rho_{\mathcal{D}}^{ac} \frac{\partial\sigma_{cb}}{\partial F_{\mathcal{D}}^{or}} + \frac{\partial\sigma_{ac}}{\partial F_{\mathcal{D}}^{or}} \rho_{\mathcal{D}}^{cb} \right) - \frac{\varepsilon_{\mathcal{A}}^{or}}{\tau_l} \sum_c \left(\rho_{\mathcal{A}}^{ac} \frac{\partial\sigma_{cb}}{\partial F_{\mathcal{A}}^{or}} + \frac{\partial\sigma_{ac}}{\partial F_{\mathcal{A}}^{or}} \rho_{\mathcal{A}}^{cb} \right) \\
& + \frac{1}{\tau_l} \frac{\partial}{\partial F_{\mathcal{D}}^{or}} \left(F_{\mathcal{D}}^{or}\sigma_{ab} + k_b T 2\varepsilon_{\mathcal{D}}^{or} \frac{\partial}{\partial F_{\mathcal{D}}^{or}} \sigma_{ab} \right) + \frac{1}{\tau_l} \frac{\partial}{\partial F_{\mathcal{A}}^{or}} \left(F_{\mathcal{A}}^{or}\sigma_{ab} + k_b T 2\varepsilon_{\mathcal{A}}^{or} \frac{\partial}{\partial F_{\mathcal{A}}^{or}} \sigma_{ab} \right), \\
\forall a, b = & 1, \dots, N,
\end{aligned} \tag{24}$$

where all quantities are defined in the main text.

In order to preserve the positivity of the density operator, we enforce a mean-field approximation setting:

$$\begin{aligned}
-\frac{\varepsilon_{\mathcal{D}}^{or}}{\tau_l} \sum_c \left(\rho_{\mathcal{D}}^{ac} \frac{\partial\sigma_{cb}}{\partial F_{\mathcal{D}}^{or}} + \frac{\partial\sigma_{ac}}{\partial F_{\mathcal{D}}^{or}} \rho_{\mathcal{D}}^{cb} \right) - \frac{\varepsilon_{\mathcal{A}}^{or}}{\tau_l} \sum_c \left(\rho_{\mathcal{A}}^{ac} \frac{\partial\sigma_{cb}}{\partial F_{\mathcal{A}}^{or}} + \frac{\partial\sigma_{ac}}{\partial F_{\mathcal{A}}^{or}} \rho_{\mathcal{A}}^{cb} \right) \simeq \\
-\frac{2\varepsilon_{\mathcal{D}}^{or}}{\tau_l} \langle \hat{\rho}_{\mathcal{D}} \rangle (F_{\mathcal{D}}^{or}) \frac{\partial\sigma_{ab}}{\partial F_{\mathcal{D}}^{or}} - \frac{2\varepsilon_{\mathcal{A}}^{or}}{\tau_l} \langle \hat{\rho}_{\mathcal{A}} \rangle (F_{\mathcal{A}}^{or}) \frac{\partial\sigma_{ab}}{\partial F_{\mathcal{A}}^{or}},
\end{aligned} \tag{25}$$

where $\langle \hat{\rho}_{\mathcal{D}(\mathcal{A})} \rangle (F_{\mathcal{D}(\mathcal{A})}^{or}) = Tr_S[\hat{\rho}_{\mathcal{D}(\mathcal{A})}\hat{\sigma}(F_{\mathcal{D}}^{or}, F_{\mathcal{A}}^{or})]$. Being interested in RET, we do not follow the complete relaxation of the system towards the ground state, so that the correction described in Eq.1 is not applied.

7 RET videos

Videos of the first 4.5 ps of the energy transfer dynamics in glassy and liquid CHCl_3 are provided. Same simulation details used in Fig.5, main text.

References

- (1) Pollard, W. T.; Friesner, R. A. Solution of the Redfield equation for the dissipative quantum dynamics of multilevel systems. *J. Chem. Phys.* **1994**, *100*, 5054–5065.
- (2) Am-Shallem, M.; Levy, A.; Schaefer, I.; Kosloff, R. Three approaches for representing Lindblad dynamics by a matrix-vector notation. *ArXiv e-prints* **2015**, arXiv:1510.08634v2 [quant-ph].
- (3) Di Maiolo, F. and Painelli, A., Intermolecular Energy Transfer in Real Time. *J. Chem. Theory Comput.* **2018**, *14*, 5339–5349.
- (4) Balzer, B.; Stock, G. Modeling of decoherence and dissipation in nonadiabatic photoreactions by an effective-scaling nonsecular Redfield algorithm. *Chem. Phys.* **2005**, *310*, 33–41.
- (5) Painelli, A. and Terenziani, F., A non-perturbative approach to solvatochromic shifts of push-pull chromophores. *Chem. Phys. Lett.* **1999**, *312*, 211 – 220.
- (6) Egorova, D.; Thoss, M.; Domcke, W.; Wang, H. Modeling of ultrafast electron-transfer processes: Validity of multilevel Redfield theory. *J. Chem. Phys.* **2003**, *119*, 2761–2773.
- (7) Egorova, D.; Domcke, W. Quantum dynamical simulations of ultrafast photoinduced electron-transfer processes. *J. Photochem. Photobiol. A: Chemistry* **2004**, *166*, 19 – 31.
- (8) Boldrini, B.; Cavalli, E.; Painelli, A.; Terenziani, F. Polar Dyes in Solution: A Joint Experimental and Theoretical Study of Absorption and Emission Band Shapes. *J. Phys. Chem. A* **2002**, *106*, 6286–6294.
- (9) Sissa, C.; Painelli, A.; Blanchard-Desce, M.; Terenziani, F. Fluorescence Anisotropy Spectra Disclose the Role of Disorder in Optical Spectra of Branched Intramolecular-Charge-Transfer Molecules. *J. Phys. Chem. B* **2011**, *115*, 7009–7020.

- (10) Painelli, A. and Terenziani, F., Linear and non-linear optical properties of push-pull chromophores: vibronic and solvation effects beyond perturbation theory. *Synth. Met.* **2001**, *124*, 171 – 173.
- (11) Beck, G. M.; Sergi, A. Quantum dynamics of a nano-rod under compression. *Phys. Lett. A* **2013**, *377*, 1047 – 1051.
- (12) Beck, G. M.; Sergi, A. Quantum dynamics in the partial Wigner picture. *J. Phys. A: Mathematical and Theoretical* **2013**, *46*, 395305.
- (13) Kapral, R. PROGRESS IN THE THEORY OF MIXED QUANTUM-CLASSICAL DYNAMICS. *Annu. Rev. Phys. Chem.* **2006**, *57*, 129–157.
- (14) Kapral, R., Quantum-Classical Dynamics in a Classical Bath. *J. Phys. Chem. A* **2001**, *105*, 2885–2889.
- (15) Mukamel, S. *Principles of nonlinear optical spectroscopy*; Oxford series in optical and imaging sciences; Oxford University Press, 1995; pp 358–359.
- (16) Davies, R. W. The Connection between the Smoluchowski Equation and the Kramers-Chandrasekhar Equation. *Phys. Rev.* **1954**, *93*, 1169–1170.
- (17) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. Subpicosecond Measurements of Polar Solvation Dynamics: Coumarin 153 Revisited. *J. Phys. Chem.* **1995**, *99*, 17311–17337.
- (18) Diósi, L. Hybrid quantum-classical master equations. *Phys. Scr.* **2014**, *T163*, 014004.
- (19) Diósi, L.; Gisin, N.; Strunz, W. T. Quantum approach to coupling classical and quantum dynamics. *Phys. Rev. A* **2000**, *61*, 022108.
- (20) Xu, R.-X.; Tian, B.-L.; Xu, J.; Shi, Q.; Yan, Y. Hierarchical quantum master equation with semiclassical Drude dissipation. *J. Chem. Phys.* **2009**, *131*, 214111.