Supporting information - The fate of molecular excited states: modeling charge-transfer dyes.

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1 Derivation of the $\Gamma^+_{db,ac}$ and $\Gamma^-_{db,ac}$ terms

1.1 Model with one molecular vibration

We assume a linear system-bath coupling $\hat{H}^{lin}_{SB} = \sum_i g_i \hat{B}_i \hat{Q}$ and we evaluate the integrand in the first row of eq. 5 (main text):

$$\begin{aligned}\langle(\hat{H}_{SB}(0))_{db}(\hat{H}_{SB}(-\tau))_{ac}\rangle_b = &\sum_i |g_i|^2 q_{db} q_{ac} \langle \hat{b}_i^\dagger \hat{b}_i(-\tau)\rangle_b \\ &+ \sum_i |g_i|^2 q_{db} q_{ac} \langle \hat{b}_i \hat{b}_i^\dagger(-\tau)\rangle_b\end{aligned} \tag{1}$$

where q_{db} and q_{ac} are the db and ac matrix elements of $\hat{Q}$ and the terms containing $\hat{b}_i^{(\dagger)}\hat{b}_j^{(\dagger)}$, $\hat{b}_i^\dagger \hat{b}_i^\dagger$ and $\hat{b}_i \hat{b}_i$ are omitted as they vanish averaging over the bath state. The first row of eq. 5 hence become:

$$\begin{aligned}\Gamma^+_{db,ac} = &\frac{q_{db}q_{ac}}{\hbar^2}\int_0^\infty d\tau e^{-i\omega_{ac}\tau}\sum_i |g_i|^2 \langle \hat{b}_i^\dagger(\tau)\hat{b}_i\rangle_b \\ &+ \frac{q_{db}q_{ac}}{\hbar^2}\int_0^\infty d\tau e^{-i\omega_{ac}\tau}\sum_i |g_i|^2 \langle \hat{b}_i(\tau)\hat{b}_i^\dagger\rangle_b\end{aligned} \tag{2}$$

where $\langle \hat{b}_i^\dagger \hat{b}_i(-\tau)\rangle_b = \langle \hat{b}_i^\dagger(\tau)\hat{b}_i\rangle_b$ and $\langle \hat{b}_i \hat{b}_i^\dagger(-\tau)\rangle_b = \langle \hat{b}_i(\tau)\hat{b}_i^\dagger\rangle_b$ follow from the smoothness in time of the bath correlation functions. Averaging over the bath equilibrium state we obtain:

$$\sum_i |g_i|^2 \langle \hat{b}_i^\dagger(\tau)\hat{b}_i\rangle_b = \sum_i |g_i|^2 e^{i\omega_i\tau}\langle \hat{n}(\omega_i)\rangle_b \tag{3}$$

$$\sum_i |g_i|^2 \langle \hat{b}_i(\tau)\hat{b}_i^\dagger\rangle_b = \sum_i |g_i|^2 e^{-i\omega_i\tau}\langle \hat{n}(\omega_i)+1\rangle_b \tag{4}$$

where $\hat{n}(\omega_i)$ is the bosonic number operator associated to the i-th bath mode, $\hat{n}(\omega_i) = \hat{b}_i^\dagger \hat{b}_i$. Introducing the form $\mathcal{I}(\omega) = \sum_i |g_i|^2 \delta(\omega - \omega_i)$ for the spectral density and substituting eq 3 and 4 in eq 2 we obtain:

$$\begin{aligned}\Gamma^{+}_{db,ac} &= \frac{q_{db}q_{ac}}{\hbar^2}\int_0^\infty d\tau e^{-i\omega_{ac}\tau}\int_0^\infty d\omega\mathcal{I}(\omega)e^{i\omega\tau}\langle\hat{n}(\omega)\rangle_b \\ &+ \frac{q_{db}q_{ac}}{\hbar^2}\int_0^\infty d\tau e^{-i\omega_{ac}\tau}\int_0^\infty d\omega\mathcal{I}(\omega)e^{-i\omega\tau}\langle\hat{n}(\omega)+1\rangle_b\end{aligned} \tag{5}$$

$$\begin{aligned}\Gamma^{+}_{db,ac} &= \frac{q_{db}q_{ac}}{\hbar^2}\int_0^\infty d\omega\mathcal{I}(\omega)\langle\hat{n}(\omega)\rangle_b\int_0^\infty d\tau e^{-i(\omega_{ac}-\omega)\tau} \\ &+ \frac{q_{db}q_{ac}}{\hbar^2}\int_0^\infty d\omega\mathcal{I}(\omega)\langle\hat{n}(\omega)+1\rangle_b\int_0^\infty d\tau e^{-i(\omega-\omega_{ca})\tau}\end{aligned} \tag{6}$$

$$\begin{aligned}\Gamma^{+}_{db,ac} &= \frac{q_{db}q_{ac}}{\hbar^2}\int_0^\infty d\omega\mathcal{I}(\omega)\langle\hat{n}(\omega)\rangle_b\left[\pi\delta(\omega_{ac}-\omega)-\frac{i}{\omega_{ac}-\omega}\right] \\ &+ \frac{q_{db}q_{ac}}{\hbar^2}\int_0^\infty d\omega\mathcal{I}(\omega)\langle\hat{n}(\omega)+1\rangle_b\left[\pi\delta(\omega-\omega_{ca})-\frac{i}{\omega-\omega_{ca}}\right]\end{aligned} \tag{7}$$

where $\delta(\omega_{ac}-\omega)$ and $\delta(\omega-\omega_{ca})$ ensures the conservation of energy. Neglecting the imaginary part of eq 7 and calculating the integrals over the frequency domain, we get:

$$\Gamma^{+}_{db,ac} = \frac{q_{db}q_{ac}}{\hbar^2}\pi\mathcal{I}(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + \frac{q_{db}q_{ac}}{\hbar^2}\pi\mathcal{I}(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b \tag{8}$$

where $\langle\hat{n}(\omega_{ac})\rangle_b = \left(e^{\frac{\hbar\omega_{ac}}{kT}}-1\right)^{-1}$ is the Bose-Einstein distribution function. Since the above integrals span positive frequencies, eq. 8 (and the analogous following expressions) has to be read as:

$$\begin{aligned}\Gamma^{+}_{db,ac} &= \frac{q_{db}q_{ac}}{\hbar^2}\pi\mathcal{I}(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b \quad \text{for} \quad \varepsilon_a > \varepsilon_c \\ \Gamma^{+}_{db,ac} &= \frac{q_{db}q_{ac}}{\hbar^2}\pi\mathcal{I}(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b \quad \text{for} \quad \varepsilon_a < \varepsilon_c\end{aligned} \tag{9}$$

while for $\varepsilon_a = \varepsilon_c$, $\Gamma^{+}_{db,ac}$ vanishes as we impose $\mathcal{I}(\omega = 0) = 0$. Similarly, for $\Gamma^{-}_{db,ac}$ we obtain:

$$\Gamma^{-}_{db,ac} = \frac{q_{db}q_{ac}}{\hbar^2}\pi\mathcal{I}(\omega_{bd})\langle\hat{n}(\omega_{bd})\rangle_b + \frac{q_{db}q_{ac}}{\hbar^2}\pi\mathcal{I}(\omega_{db})\langle\hat{n}(\omega_{db})+1\rangle_b \tag{10}$$

An analogous derivation for $\hat{H}'_{SB} = \sum_i g_i\left(\hat{b}_i^\dagger\hat{d}+\hat{b}_i\hat{d}^\dagger\right)$, referred to as the rotating wave approximation (RWA) in the main text, leads to the following expressions:

$$\Gamma^{+}_{db,ac} = \frac{\pi}{\hbar^2}\left[d_{db}d^\dagger_{ac}\mathcal{I}(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + d^\dagger_{db}d_{ac}\mathcal{I}(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b\right] \tag{11}$$

$$\Gamma^{-}_{db,ac} = \frac{\pi}{\hbar^2}\left[d_{db}d^\dagger_{ac}\mathcal{I}(\omega_{bd})\langle\hat{n}(\omega_{bd})\rangle_b + d^\dagger_{db}d_{ac}\mathcal{I}(\omega_{db})\langle\hat{n}(\omega_{db})+1\rangle_b\right] \tag{12}$$

1.2 Model with two molecular vibrations

For a system with two vibrational coordinates ($\hat{Q}_1 = \left(\hat{d}_1^\dagger + \hat{d}_1\right)/\sqrt{2}$ and $\hat{Q}_2 = \left(\hat{d}_2^\dagger + \hat{d}_2\right)/\sqrt{2}$) linearly coupled to two independent Redfield baths, the system-bath interaction hamiltonian reads $\hat{H}_{SB} = \sum_i g_i \hat{B}_{i,1}\hat{Q}^1 + \sum_j f_j \hat{B}_{j,2}\hat{Q}^2$. Two spectral densities are defined as $\mathcal{I}_1(\omega) = \sum_i |g_i|^2\delta(\omega-\omega_i)$ and $\mathcal{I}_2(\omega) = \sum_j |f_j|^2\delta(\omega-\omega_j)$. The same derivation shown above leads to:

$$\begin{aligned}\Gamma^+_{db,ac} = &\frac{\pi}{\hbar^2} q^1_{db} q^1_{ac} \left[\mathcal{I}_1(\omega_{ac})\langle \hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_1(\omega_{ca})\langle \hat{n}(\omega_{ca}) + 1\rangle_b\right] \\ &+ \frac{\pi}{\hbar^2} q^2_{db} q^2_{ac} \left[\mathcal{I}_2(\omega_{ac})\langle \hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_2(\omega_{ca})\langle \hat{n}(\omega_{ca}) + 1\rangle_b\right]\end{aligned} \tag{13}$$

$$\begin{aligned}\Gamma^-_{db,ac} = &\frac{\pi}{\hbar^2} q^1_{db} q^1_{ac} \left[\mathcal{I}_1(\omega_{bd})\langle \hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_1(\omega_{db})\langle \hat{n}(\omega_{db}) + 1\rangle_b\right] \\ &+ \frac{\pi}{\hbar^2} q^2_{db} q^2_{ac} \left[\mathcal{I}_2(\omega_{bd})\langle \hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_2(\omega_{db})\langle \hat{n}(\omega_{db}) + 1\rangle_b\right]\end{aligned} \tag{14}$$

where we wrote $\hat{n}(\omega_{ac})\rangle_{b1} = \hat{n}(\omega_{ac})\rangle_{b2} = \hat{n}(\omega_{ac})\rangle_b$ since the Bose-Einstein distribution depends only on the temperature, which of course is the same for the two baths. When the two coordinates are linearly coupled to the same Redfield bath the interaction hamiltonian reads $\hat{H}_{SB} = \sum_i \hat{B}_i \left(g_i\hat{Q}^1 + f_i\hat{Q}^2\right)$. Two additional spectral density functions have to be defined as $\mathcal{I}_{12}(\omega) = \sum_i g_i f_i^* \delta(\omega-\omega_i)$ and $\mathcal{I}_{21}(\omega) = \sum_i g_i^* f_i \delta(\omega-\omega_i)$, and since g and f are real and positive for every bath oscillator, then $\mathcal{I}_{12}(\omega) = \mathcal{I}_{21}(\omega) = \sqrt{\mathcal{I}_1(\omega)\mathcal{I}_2(\omega)}$. In this case, expressions for $\Gamma^+_{db,ac}$ and $\Gamma^-_{db,ac}$ read:

$$\begin{aligned}\Gamma^+_{db,ac} = &\frac{\pi}{\hbar^2} q^1_{db} q^1_{ac} \left[\mathcal{I}_1(\omega_{ac})\langle \hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_1(\omega_{ca})\langle \hat{n}(\omega_{ca}) + 1\rangle_b\right] \\ &+ \frac{\pi}{\hbar^2} q^2_{db} q^2_{ac} \left[\mathcal{I}_2(\omega_{ac})\langle \hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_2(\omega_{ca})\langle \hat{n}(\omega_{ca}) + 1\rangle_b\right] \\ &+ \frac{\pi}{\hbar^2} q^1_{db} q^2_{ac} \left[\mathcal{I}_{12}(\omega_{ac})\langle \hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_{12}(\omega_{ca})\langle \hat{n}(\omega_{ca}) + 1\rangle_b\right] \\ &+ \frac{\pi}{\hbar^2} q^2_{db} q^1_{ac} \left[\mathcal{I}_{12}(\omega_{ac})\langle \hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_{12}(\omega_{ca})\langle \hat{n}(\omega_{ca}) + 1\rangle_b\right]\end{aligned} \tag{15}$$

$$\begin{aligned}\Gamma^-_{db,ac} = &\frac{\pi}{\hbar^2} q^1_{db} q^1_{ac} \left[\mathcal{I}_1(\omega_{bd})\langle \hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_1(\omega_{db})\langle \hat{n}(\omega_{db}) + 1\rangle_b\right] \\ &+ \frac{\pi}{\hbar^2} q^2_{db} q^2_{ac} \left[\mathcal{I}_2(\omega_{bd})\langle \hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_2(\omega_{db})\langle \hat{n}(\omega_{db}) + 1\rangle_b\right] \\ &+ \frac{\pi}{\hbar^2} q^1_{db} q^2_{ac} \left[\mathcal{I}_{12}(\omega_{bd})\langle \hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_{12}(\omega_{db})\langle \hat{n}(\omega_{db}) + 1\rangle_b\right] \\ &+ \frac{\pi}{\hbar^2} q^2_{db} q^1_{ac} \left[\mathcal{I}_{12}(\omega_{bd})\langle \hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_{12}(\omega_{db})\langle \hat{n}(\omega_{db}) + 1\rangle_b\right]\end{aligned} \tag{16}$$

Expressions are also derived within the RWA. When each coordinate is coupled to an independent bath, they read:

$$\begin{aligned}\Gamma^{+}_{db,ac} = \frac{\pi}{\hbar^2} \Big[& d^1_{db} d^{1\dagger}_{ac} \mathcal{I}_1(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{1\dagger}_{db} d^1_{ac} \mathcal{I}_1(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\ & + d^2_{db} d^{2\dagger}_{ac} \mathcal{I}_2(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{2\dagger}_{db} d^2_{ac} \mathcal{I}_2(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \Big]\end{aligned} \tag{17}$$

$$\begin{aligned}\Gamma^{-}_{db,ac} = \frac{\pi}{\hbar^2} \Big[& d^1_{db} d^{1\dagger}_{ac} \mathcal{I}_1(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{1\dagger}_{db} d^1_{ac} \mathcal{I}_1(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\ & + d^2_{db} d^{2\dagger}_{bd} \mathcal{I}_2(\omega_{bd}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{2\dagger}_{db} d^2_{ac} \mathcal{I}_2(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \Big]\end{aligned} \tag{18}$$

whereas, when both coordinates are coupled to the same bath we have:

$$\begin{aligned}\Gamma^{+}_{db,ac} = \frac{\pi}{\hbar^2} \Big[& d^1_{db} d^{1\dagger}_{ac} \mathcal{I}_1(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{1\dagger}_{db} d^1_{ac} \mathcal{I}_1(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\ & + d^2_{db} d^{2\dagger}_{ac} \mathcal{I}_2(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{2\dagger}_{db} d^2_{ac} \mathcal{I}_2(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\ & + d^1_{db} d^{2\dagger}_{ac} \mathcal{I}_{12}(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{1\dagger}_{db} d^2_{ac} \mathcal{I}_{12}(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\ & + d^2_{db} d^{1\dagger}_{ac} \mathcal{I}_{12}(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{2\dagger}_{db} d^1_{ac} \mathcal{I}_{12}(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \Big]\end{aligned} \tag{19}$$

$$\begin{aligned}\Gamma^{-}_{db,ac} = \frac{\pi}{\hbar^2} \Big[& d^1_{db} d^{1\dagger}_{ac} \mathcal{I}_1(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{1\dagger}_{db} d^1_{ac} \mathcal{I}_1(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\ & + d^2_{db} d^{2\dagger}_{ac} \mathcal{I}_2(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{2\dagger}_{db} d^2_{ac} \mathcal{I}_2(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\ & + d^1_{db} d^{2\dagger}_{ac} \mathcal{I}_{12}(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{1\dagger}_{db} d^2_{ac} \mathcal{I}_{12}(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\ & + d^2_{db} d^{1\dagger}_{ac} \mathcal{I}_{12}(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{2\dagger}_{db} d^1_{ac} \mathcal{I}_{12}(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \Big]\end{aligned} \tag{20}$$

1.3 Model with three molecular vibrations

The treatment is extended also to a model with three molecular vibrations, leading to the following expressions for the different cases.

Three coordinates linearly coupled to three independent baths:

$$\begin{aligned}\Gamma^{+}_{db,ac} = & \frac{\pi}{\hbar^2} q^1_{db} q^1_{ac} \left[\mathcal{I}_1(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + \mathcal{I}_1(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \right] \\ & + \frac{\pi}{\hbar^2} q^2_{db} q^2_{ac} \left[\mathcal{I}_2(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + \mathcal{I}_2(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \right] \\ & + \frac{\pi}{\hbar^2} q^3_{db} q^3_{ac} \left[\mathcal{I}_3(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + \mathcal{I}_3(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \right]\end{aligned} \tag{21}$$

$$\begin{aligned}\Gamma^{-}_{db,ac} = & \frac{\pi}{\hbar^2} q^1_{db} q^1_{ac} \left[\mathcal{I}_1(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + \mathcal{I}_1(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \right] \\ & + \frac{\pi}{\hbar^2} q^2_{db} q^2_{ac} \left[\mathcal{I}_2(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + \mathcal{I}_2(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \right] \\ & + \frac{\pi}{\hbar^2} q^3_{db} q^3_{ac} \left[\mathcal{I}_3(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + \mathcal{I}_3(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \right]\end{aligned} \tag{22}$$

Three coordinates linearly coupled to the same bath:

$$
\begin{aligned}
\Gamma^{+}_{db,ac} = {} & \frac{\pi}{\hbar^2} q^1_{db} q^1_{ac} \left[\mathcal{I}_1(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_1(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^2_{db} q^2_{ac} \left[\mathcal{I}_2(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_2(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^3_{db} q^3_{ac} \left[\mathcal{I}_3(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_3(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^1_{db} q^2_{ac} \left[\mathcal{I}_{12}(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_{12}(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^2_{db} q^1_{ac} \left[\mathcal{I}_{12}(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_{12}(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^1_{db} q^3_{ac} \left[\mathcal{I}_{13}(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_{13}(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^3_{db} q^1_{ac} \left[\mathcal{I}_{13}(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_{13}(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^2_{db} q^3_{ac} \left[\mathcal{I}_{23}(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_{23}(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^3_{db} q^2_{ac} \left[\mathcal{I}_{23}(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + \mathcal{I}_{23}(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b\right]
\end{aligned} \tag{23}
$$

$$
\begin{aligned}
\Gamma^{-}_{db,ac} = {} & \frac{\pi}{\hbar^2} q^1_{db} q^1_{ac} \left[\mathcal{I}_1(\omega_{bd})\langle\hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_1(\omega_{db})\langle\hat{n}(\omega_{db})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^2_{db} q^2_{ac} \left[\mathcal{I}_2(\omega_{bd})\langle\hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_2(\omega_{db})\langle\hat{n}(\omega_{db})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^3_{db} q^3_{ac} \left[\mathcal{I}_3(\omega_{bd})\langle\hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_3(\omega_{db})\langle\hat{n}(\omega_{db})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^1_{db} q^2_{ac} \left[\mathcal{I}_{12}(\omega_{bd})\langle\hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_{12}(\omega_{db})\langle\hat{n}(\omega_{db})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^2_{db} q^1_{ac} \left[\mathcal{I}_{12}(\omega_{bd})\langle\hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_{12}(\omega_{db})\langle\hat{n}(\omega_{db})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^1_{db} q^3_{ac} \left[\mathcal{I}_{13}(\omega_{bd})\langle\hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_{13}(\omega_{db})\langle\hat{n}(\omega_{db})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^3_{db} q^1_{ac} \left[\mathcal{I}_{13}(\omega_{bd})\langle\hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_{13}(\omega_{db})\langle\hat{n}(\omega_{db})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^2_{db} q^3_{ac} \left[\mathcal{I}_{23}(\omega_{bd})\langle\hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_{23}(\omega_{db})\langle\hat{n}(\omega_{db})+1\rangle_b\right] \\
& + \frac{\pi}{\hbar^2} q^3_{db} q^2_{ac} \left[\mathcal{I}_{23}(\omega_{bd})\langle\hat{n}(\omega_{bd})\rangle_b + \mathcal{I}_{23}(\omega_{db})\langle\hat{n}(\omega_{db})+1\rangle_b\right]
\end{aligned} \tag{24}
$$

RWA with three coordinates coupled to three independent baths:

$$
\begin{aligned}
\Gamma^{+}_{db,ac} = \frac{\pi}{\hbar^2} \Big[& d^1_{db} d^{1\dagger}_{ac} \mathcal{I}_1(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + d^{1\dagger}_{db} d^1_{ac} \mathcal{I}_1(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b \\
& + d^2_{db} d^{2\dagger}_{ac} \mathcal{I}_2(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + d^{2\dagger}_{db} d^2_{ac} \mathcal{I}_2(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b \\
& + d^3_{db} d^{3\dagger}_{ac} \mathcal{I}_3(\omega_{ac})\langle\hat{n}(\omega_{ac})\rangle_b + d^{3\dagger}_{db} d^3_{ac} \mathcal{I}_3(\omega_{ca})\langle\hat{n}(\omega_{ca})+1\rangle_b \Big]
\end{aligned} \tag{25}
$$

$$
\begin{aligned}
\Gamma^{-}_{db,ac} = \frac{\pi}{\hbar^2} \Big[& d^{1}_{db} d^{1\dagger}_{ac} \mathcal{I}_1(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{1\dagger}_{db} d^{1}_{ac} \mathcal{I}_1(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\
& + d^{2}_{db} d^{2\dagger}_{ac} \mathcal{I}_2(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{2\dagger}_{db} d^{2}_{ac} \mathcal{I}_2(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\
& + d^{3}_{db} d^{3\dagger}_{ac} \mathcal{I}_3(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{3\dagger}_{db} d^{3}_{ac} \mathcal{I}_3(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \Big]
\end{aligned} \tag{26}
$$

RWA with three coordinates coupled to the same bath:

$$
\begin{aligned}
\Gamma^{+}_{db,ac} = \frac{\pi}{\hbar^2} \Big[& d^{1}_{db} d^{1\dagger}_{ac} \mathcal{I}_1(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{1\dagger}_{db} d^{1}_{ac} \mathcal{I}_1(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\
& + d^{2}_{db} d^{2\dagger}_{ac} \mathcal{I}_2(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{2\dagger}_{db} d^{2}_{ac} \mathcal{I}_2(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\
& + d^{3}_{db} d^{3\dagger}_{ac} \mathcal{I}_3(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{3\dagger}_{db} d^{3}_{ac} \mathcal{I}_3(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\
& + d^{1}_{db} d^{2\dagger}_{ac} \mathcal{I}_{12}(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{1\dagger}_{db} d^{2}_{ac} \mathcal{I}_{12}(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\
& + d^{2}_{db} d^{1\dagger}_{ac} \mathcal{I}_{12}(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{2\dagger}_{db} d^{1}_{ac} \mathcal{I}_{12}(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\
& + d^{1}_{db} d^{3\dagger}_{ac} \mathcal{I}_{13}(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{1\dagger}_{db} d^{3}_{ac} \mathcal{I}_{13}(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\
& + d^{3}_{db} d^{1\dagger}_{ac} \mathcal{I}_{13}(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{3\dagger}_{db} d^{1}_{ac} \mathcal{I}_{13}(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\
& + d^{2}_{db} d^{3\dagger}_{ac} \mathcal{I}_{23}(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{2\dagger}_{db} d^{3}_{ac} \mathcal{I}_{23}(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \\
& + d^{3}_{db} d^{2\dagger}_{ac} \mathcal{I}_{23}(\omega_{ac}) \langle \hat{n}(\omega_{ac}) \rangle_b + d^{3\dagger}_{db} d^{2}_{ac} \mathcal{I}_{23}(\omega_{ca}) \langle \hat{n}(\omega_{ca}) + 1 \rangle_b \Big]
\end{aligned} \tag{27}
$$

$$
\begin{aligned}
\Gamma^{-}_{db,ac} = \frac{\pi}{\hbar^2} \Big[& d^{1}_{db} d^{1\dagger}_{ac} \mathcal{I}_1(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{1\dagger}_{db} d^{1}_{ac} \mathcal{I}_1(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\
& + d^{2}_{db} d^{2\dagger}_{ac} \mathcal{I}_2(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{2\dagger}_{db} d^{2}_{ac} \mathcal{I}_2(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\
& + d^{3}_{db} d^{3\dagger}_{ac} \mathcal{I}_3(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{3\dagger}_{db} d^{3}_{ac} \mathcal{I}_3(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\
& + d^{1}_{db} d^{2\dagger}_{ac} \mathcal{I}_{12}(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{1\dagger}_{db} d^{2}_{ac} \mathcal{I}_{12}(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\
& + d^{2}_{db} d^{1\dagger}_{ac} \mathcal{I}_{12}(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{2\dagger}_{db} d^{1}_{ac} \mathcal{I}_{12}(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\
& + d^{1}_{db} d^{3\dagger}_{ac} \mathcal{I}_{13}(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{1\dagger}_{db} d^{3}_{ac} \mathcal{I}_{13}(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\
& + d^{3}_{db} d^{1\dagger}_{ac} \mathcal{I}_{13}(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{3\dagger}_{db} d^{1}_{ac} \mathcal{I}_{13}(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\
& + d^{2}_{db} d^{3\dagger}_{ac} \mathcal{I}_{23}(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{2\dagger}_{db} d^{3}_{ac} \mathcal{I}_{23}(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \\
& + d^{3}_{db} d^{2\dagger}_{ac} \mathcal{I}_{23}(\omega_{bd}) \langle \hat{n}(\omega_{bd}) \rangle_b + d^{3\dagger}_{db} d^{2}_{ac} \mathcal{I}_{23}(\omega_{db}) \langle \hat{n}(\omega_{db}) + 1 \rangle_b \Big]
\end{aligned} \tag{28}
$$

2 Debye spectral density and RWA

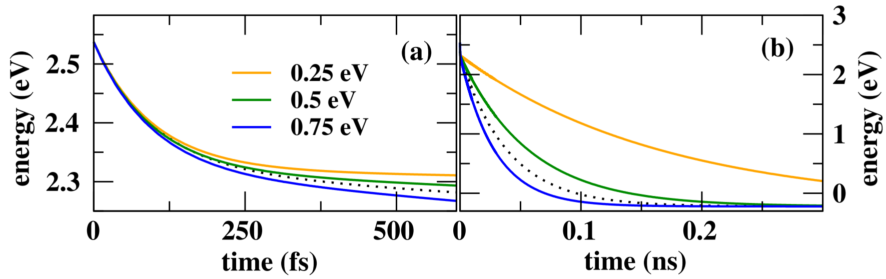

Figure 1: The same as the top panels of Fig. 4 (main text), but imposing the RWA in the system-bath coupling.

3 Results for multimode systems

Calculations for the model with 2 vibrational coordinates are obtained exploiting the pseudo non-secular approximation (i.e., keeping only the non-secular $R_{ab,cd}$ terms for which $|\omega_{ab} - \omega_{cd}| \leq \alpha$, with $\alpha = 0.01$ eV). Calculations for the model with 3 coordinates are performed adopting the secular approximation (i.e., keeping only the $R_{ab,cd}$ terms satisfying the resonance condition $|\omega_{ab} - \omega_{cd}| = 0$).

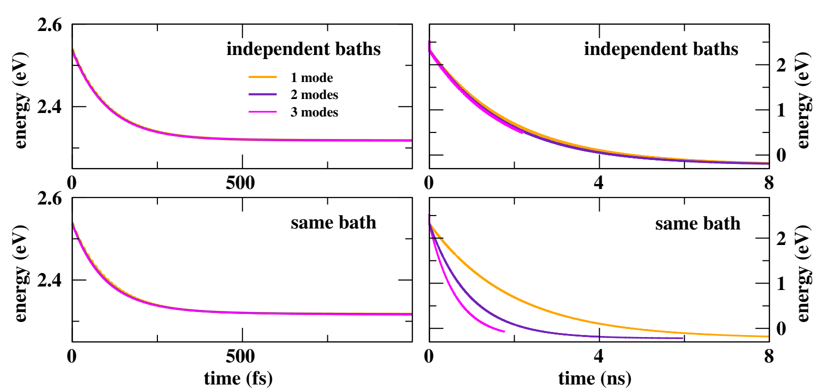

Figure 2: Time-evolution of energy calculated for DCM imposing a constant spectral density and linear system-bath coupling. Results for the model with one (orange lines), two (purple lines) and three (magenta lines) vibrational coordinates. Top panels show results obtained coupling each coordinate with an independent Redfield bath, bottom panels show results obtained coupling all the coordinates with the same Redfield bath. Zero point energies of the additional modes are subtracted in order to have the energy on the same scale.

The parameters used in the calculation with one and two molecular vibrations were already reported in the main text. For the model with three coordinates, the parameters (in eV) read: $z_0 = 1.14$, $\tau = 0.88$, $\varepsilon_1 = 0.12$, $\hbar\omega_1 = 0.146$, $\varepsilon_2 = 0.152$, $\hbar\omega_2 = 0.17$, $\varepsilon_3 = 0.184$, $\hbar\omega_3 = 0.2$.

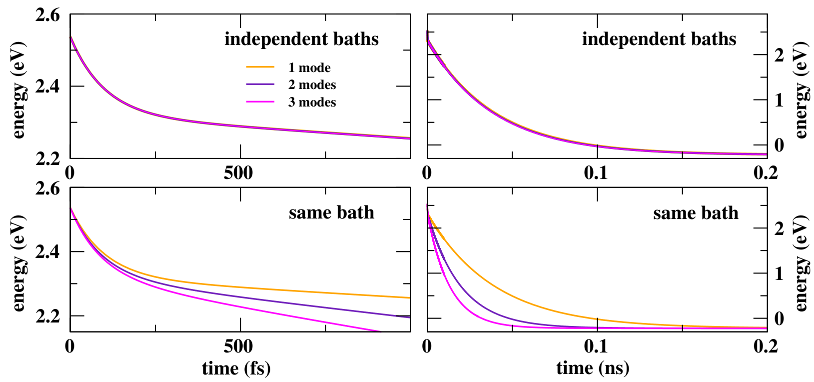

Figure 3: Same quantities as in figure 2 adopting the RWA in the system-bath coupling.

4 Results for other dyes

		z_0	$-\tau$	ε_{v1}	$\hbar\omega_{v1}$	ε_{v2}	$\hbar\omega_{v2}$
$C_{16}H_{33}Q$-3CNQ	1 mode	-0.25	0.47	0.17	0.14	-	-
	2 modes	-0.25	0.47	0.08	0.13	0.09	0.15
Nile Red	1 mode	0.88	0.95	0.33	0.14	-	-
	2 modes	0.88	0.95	0.15	0.135	0.18	0.145
DANS	1 mode	1.32	0.72	0.3	0.17	-	-
	2 modes	1.32	0.72	0.12	0.15	0.18	0.19

Table 1: Molecular parameters for $C_{16}H_{33}Q$-3CNQ, Nile Red and DANS for the model with one and two vibrational coordinates (all the quantities in eV).

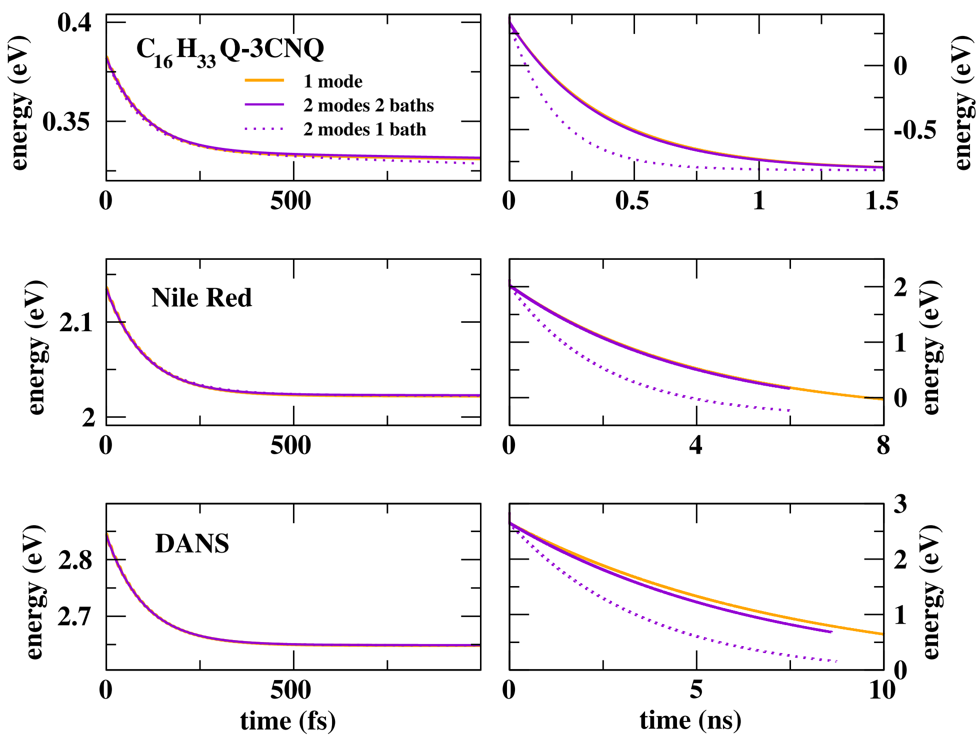

Figure 4: Energy vs time for $C_{16}H_{33}$Q-3CNQ, Nile Red and DANS imposing a constant spectral density ($\gamma = 5$ ps^{-1}) and linear system-bath coupling. Results for the model with one vibrational coordinate (orange lines), with two coordinates coupled to two independent baths (purple continuous lines) and with two coordinates coupled to the same bath (purple dotted lines) are shown.