Nonadiabatic Coupling Reduces the Activation Energy in Thermally Activated Delayed Fluorescence: Supporting Information

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S1   Linear Spin Vibronic Model Hamiltonian

The Hamiltonian used in the present work is based upon a Linear spin-vibronic coupling Hamiltonian described in ref. [1, 2]. Briefly, it has the general form:

$$
\hat{H} = \begin{pmatrix}
\frac{\omega}{2}\left(\frac{\partial^2}{\partial Q_i^2} + Q_i^2\right) + E^{rel}_{3LE} & \lambda_{Q_i} & E_{SOC} \\
\lambda_{Q_i} & \frac{\omega}{2}\left(\frac{\partial^2}{\partial Q_i^2} + Q_i^2\right) + E^{rel}_{3CT} & E_{HFI} \\
E_{SOC} & E_{HFI} & \frac{\omega}{2}\left(\frac{\partial^2}{\partial Q_i^2} + Q_i^2\right) + E^{rel}_{1CT}
\end{pmatrix}
\tag{S1}
$$

where Q_i is the nuclear degree of freedom and E^{rel} is the excited state energy, relative to the ^3LE state. This means that E^{rel}_{3LE} will be 0, while for E^{rel}_{3CT} and E^{rel}_{1CT}, the energy represents the gap between this state and the ^3LE state. The expansion coefficients used are shown in Table S1

Parameter	
ω_1	13.60
ω_{11}	173.65
ω_{23}	422.60
E^{rel}_{3LE} (eV)	0.00
E^{rel}_{3CT} (eV)	0.07 (0.03)
E^{rel}_{1CT} (eV)	0.10 (0.06)
E_{SOC}	2.00
E_{HFI}	0.20
λ_1	67.02 (134.04)
λ_{11}	91.71 (183.42)
λ_{23}	79.04 (158.08)

Table S1: Hamiltonian parameters for each ρMCTDH simulation. All energies are in cm^{-1} unless stated otherwise. In brackets are values that are altered as described in the manuscript.

S2   Quantum Dynamics Simulations

We perform simulations within a density operator formalism of MCTDH [3]. Here the single particle functions are replaced with single-particle density operators. Here we adopt a closed quantum system, this is to say that no dissipative operators are included and only the core Hamiltonian described above is used. In this representation the Liouville-von Neumann equation for the system is expressed:

$$
\dot{\rho}(t) = -\frac{i}{\hbar}[H, \rho(t)]
\tag{S2}
$$

Although the model Hamiltonian used herein is relatively small, for the density operator simulations the dimensionality of the system formally doubles [4] significantly increasing the numerical treatment of the simulations. The full details of the details of the MCTDH simulations are given in Table S2 and ensure convergence for the population kinetics for the entire simulations of 250 ps.

Table S2: Computational details for the MCTDH simulations within both the wavefunction and density operator formalisms. N_i is the number of primitive harmonic oscillator discrete variable representation (DVR) basis functions used to describe each mode. n_i are the number of single-particle functions used to describe the wavepacket on each state.

	Modes	N_i	n_{S_1},n_{T_1},n_{T_2}
Density Operator	ν_1,ν_{11}	21	21,61,41
	ν_{23}	21	12,12,12

The dynamics were performed using the model Hamiltonian described above. The computational details for the quantum dynamics simulations are shown in Table S1 and ensured convergence of the population kinetics shown in the main text.

References

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