Supporting Information for Enhancing Triplet Harvesting in Inverted Singlet-Triplet Gap Molecules through Mechanistic Understanding

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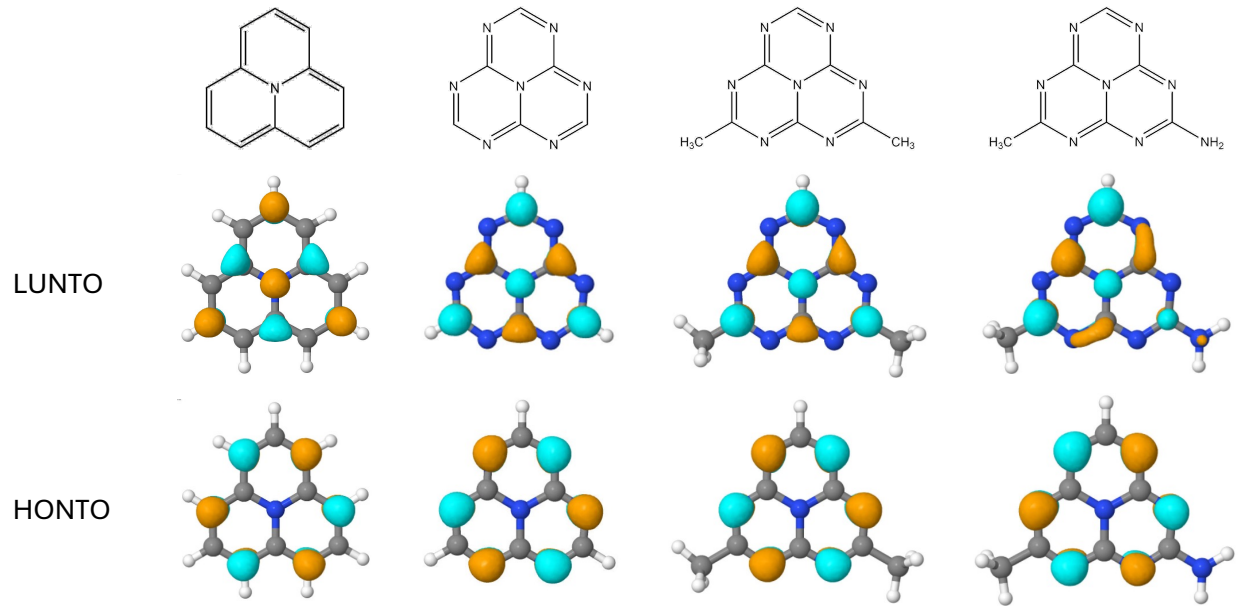

Figure S1: Highest Occupied Natural Transition Orbitals (HONTO) and Lowest Unoccupied Natural Transition Orbitals (LUNTO) of molecules **1**, **2**, **3**, and **4** at their equilibrium ground state geometry.

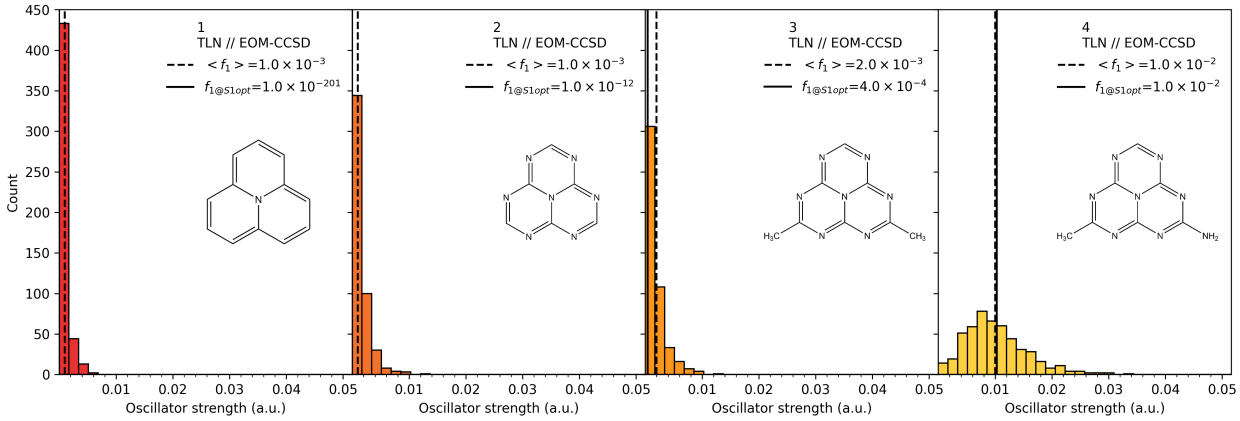

Figure S2: Distribution of oscillator strengths for molecules **1** to **4** in the S_1 ensemble. Vertical dashed lines show the ensemble average whereas solid vertical lines show values for optimized structures.

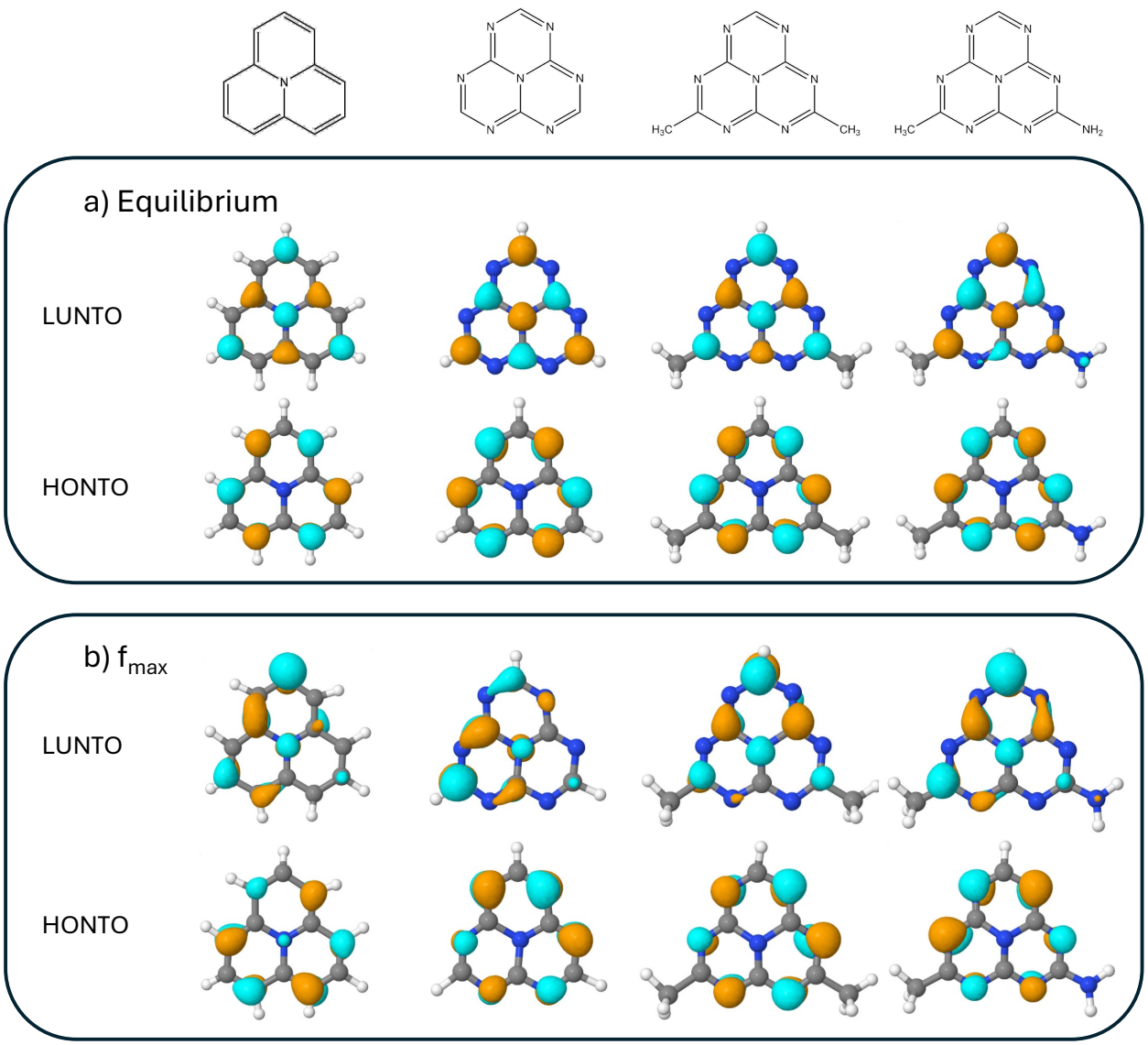

Figure S3: Natural transition orbitals of molecules **1**, **2**, **3**, and **4** at a) S_1 equilibrium geometries, b) Geometries with the highest oscillator strength in the S_1 ensemble.

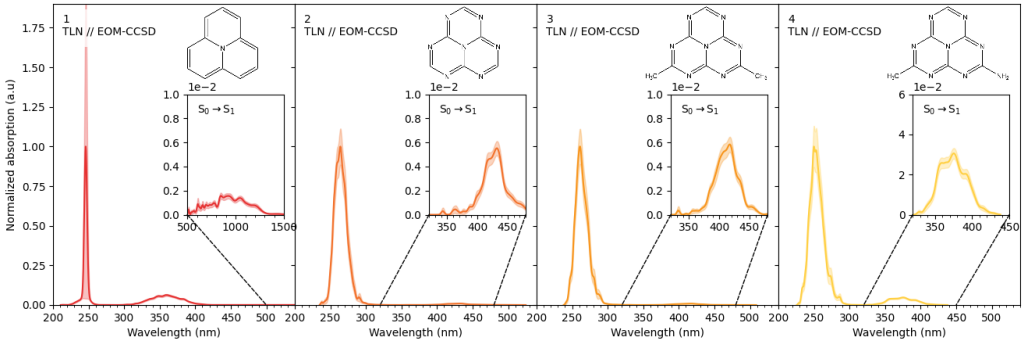

Figure S4: Normalized absorption spectra of molecules **1** to **4**. The inset displays the absorption spectrum corresponding to the first singlet excited state, $S_0 \rightarrow S_1$, computed using EOM-CCSD/cc-pVDZ in toluene.

Table S1: Calculated rate constants of electronic transitions ($k_{i\to f}$), quantum yields (ϕ), average energy gaps (ΔE), and average spin-orbit couplings (<SOC>).

Transition	$\boldsymbol{k_{i\to f}}$ **[s^{-1}]**	ϕ **[(%)]**	Δ**E [eV]**	<**SOC**> **[meV]**
		1		
$S_1 \to S_0$	$(9.0 \pm 0.5) \times 10^4$	99	1.013	-
$S_1 \rightsquigarrow T_1$	$(4.1 \pm 0.4) \times 10^7$	100	-0.021	0.028
$S_1 \rightsquigarrow T_2$	$(3 \pm 3) \times 10^{-59}$	0	1.077	0.094
$T_1 \to S_0$	$(1.1 \pm 0.8) \times 10^3$	1	1.059	-
$T_1 \rightsquigarrow S_0$	$(5 \pm 5) \times 10^{-49}$	0	1.059	0.383
$T_1 \rightsquigarrow S_1$	$(3.5 \pm 0.3) \times 10^7$	100	0.013	0.029
		2		
$S_1 \to S_0$	$(8.6 \pm 0.5) \times 10^5$	97	2.426	-
$S_1 \rightsquigarrow T_1$	$(2.2 \pm 0.5) \times 10^7$	96	-0.136	0.033
$S_1 \rightsquigarrow T_2$	$(3 \pm 2) \times 10^{-57}$	0	1.029	0.504
$T_1 \to S_0$	$(5 \pm 3) \times 10^4$	3	2.564	-
$T_1 \rightsquigarrow S_0$	0 ± 0	0	2.564	0.631
$T_1 \rightsquigarrow S_1$	$(3.5 \pm 0.6) \times 10^7$	100	-0.111	0.036
		3		
$S_1 \to S_0$	$(1.03 \pm 0.05) \times 10^6$	93	2.475	-
$S_1 \rightsquigarrow T_1$	$(1.6 \pm 0.4) \times 10^7$	94	-0.147	0.033
$S_1 \rightsquigarrow T_2$	$(2 \pm 2) \times 10^{-6}$	0	1.046	0.586
$T_1 \to S_0$	$(2 \pm 2) \times 10^5$	7	2.339	-
$T_1 \rightsquigarrow S_0$	$(3 \pm 3) \times 10^{-30}$	0	2.339	0.577
$T_1 \rightsquigarrow S_1$	$(5 \pm 1) \times 10^7$	100	-0.114	0.044
		4		
$S_1 \to S_0$	$(7.4 \pm 0.2) \times 10^6$	95	2.727	-
$S_1 \rightsquigarrow T_1$	$(5.1 \pm 0.9) \times 10^7$	87	-0.093	0.038
$S_1 \rightsquigarrow T_2$	$(7 \pm 7) \times 10^2$	0	0.925	1.106
$T_1 \to S_0$	$(4 \pm 3) \times 10^5$	5	2.905	-
$T_1 \rightsquigarrow S_0$	0 ± 0	0	2.905	0.666
$T_1 \rightsquigarrow S_1$	$(5.6 \pm 0.5) \times 10^7$	99	0.028	0.040

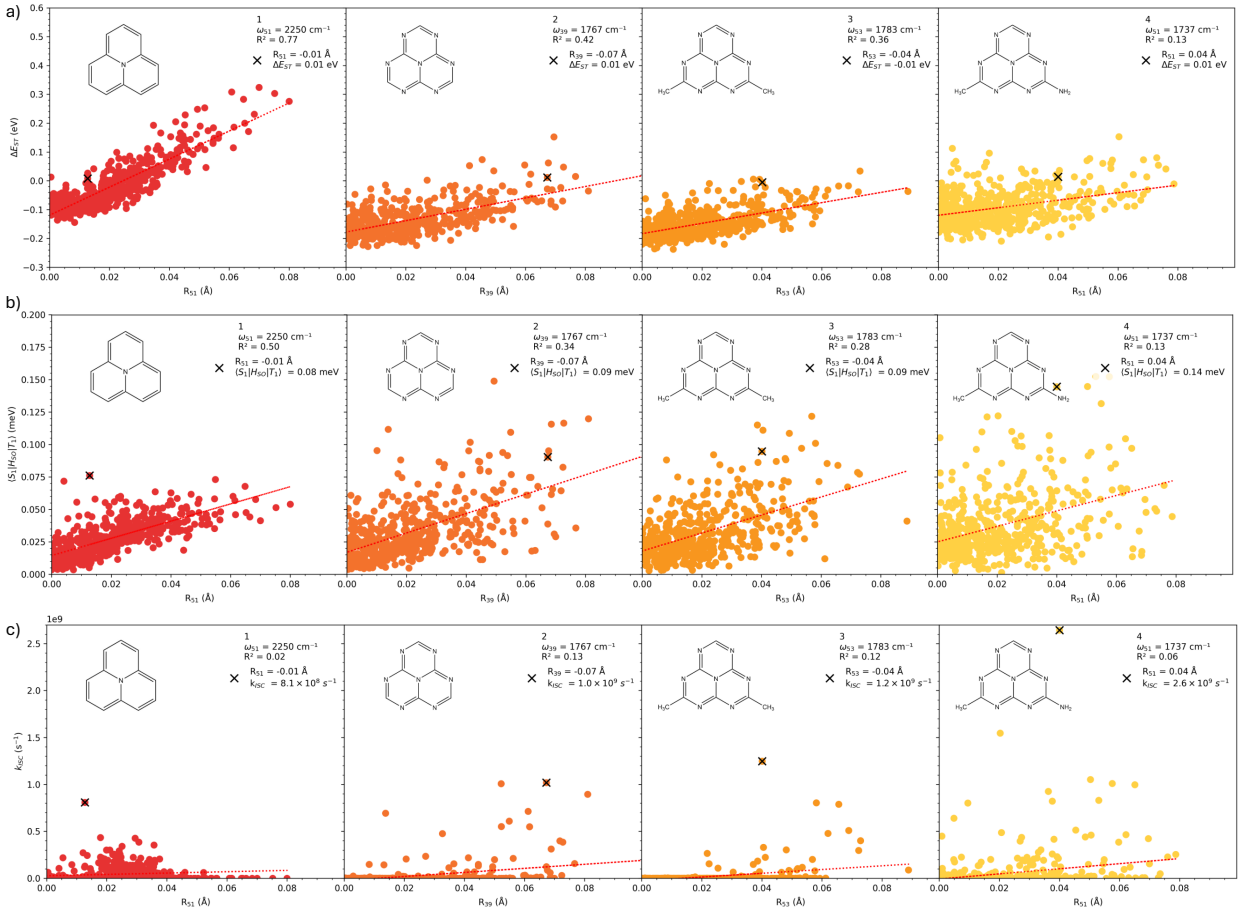

Figure S5: Correlation between the nuclear displacement along the i^{th} vibrational mode (R_i) and a) ΔE_{ST}, b) $\langle S_1|H_{SO}|T_1\rangle$ (meV), and c) k_{isc}. The black cross corresponds to the parameter for the geometry that contributes the most to k_{ISC} for each system. For each molecule, there is only one mode with significant correlation.

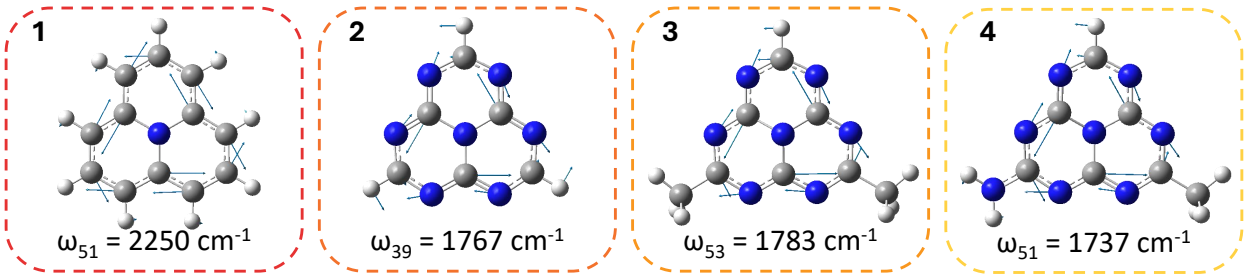

Figure S6: Vibrational mode that has the highest correlation between the amplitude of nuclear displacement and both, ΔE_{ST} and $\langle S_1|H_{SO}|T_1\rangle$.

Simulated time-resolved photoluminescence spectra

For simulations of time-resolved spectra, we employ the following kinetic model:

$$\frac{dS_1}{dt} = -(k_F + k_{ISC})S_1 + k_{rISC}T_1 \tag{S1}$$

$$\frac{dT_1}{dt} = k_{ISC}S_1 - (k_P + k_{rISC} + k_{nr})T_1 \tag{S2}$$

$$\frac{dS_{0(em)}}{dt} = k_F S_1 + k_P T_1 \tag{S3}$$

$$\frac{dS_{0(nem)}}{dt} = k_{nr}T_1 \tag{S4}$$

Here, the emissive (em) and non-emissive (nem) pathways to the ground state were separated. In Equation S4, k_F and k_P are the fluorescence and phosphorescence rates and k_{nr}, k_{ISC} and k_{rISC} are the ISC rates from T_1 to S_0, $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_1$, respectively.

The above equation can be written in a matrix form such that

$$\frac{dP(t)}{dt} = MP(t), \tag{S5}$$

where $P(t)$ is the population vector, a column vector composed of $(S_1, T_1, S_{0(em)}, S_{0(nr)})$. This equation has a solution $P(t) = \exp(Mt)P(0)$, from which S_1 and T_1 population curves can be plotted as a function of time. The time-resolved photoluminescence spectrum is obtained by computing $\frac{dS_{0(em)}(t)}{dt}$.

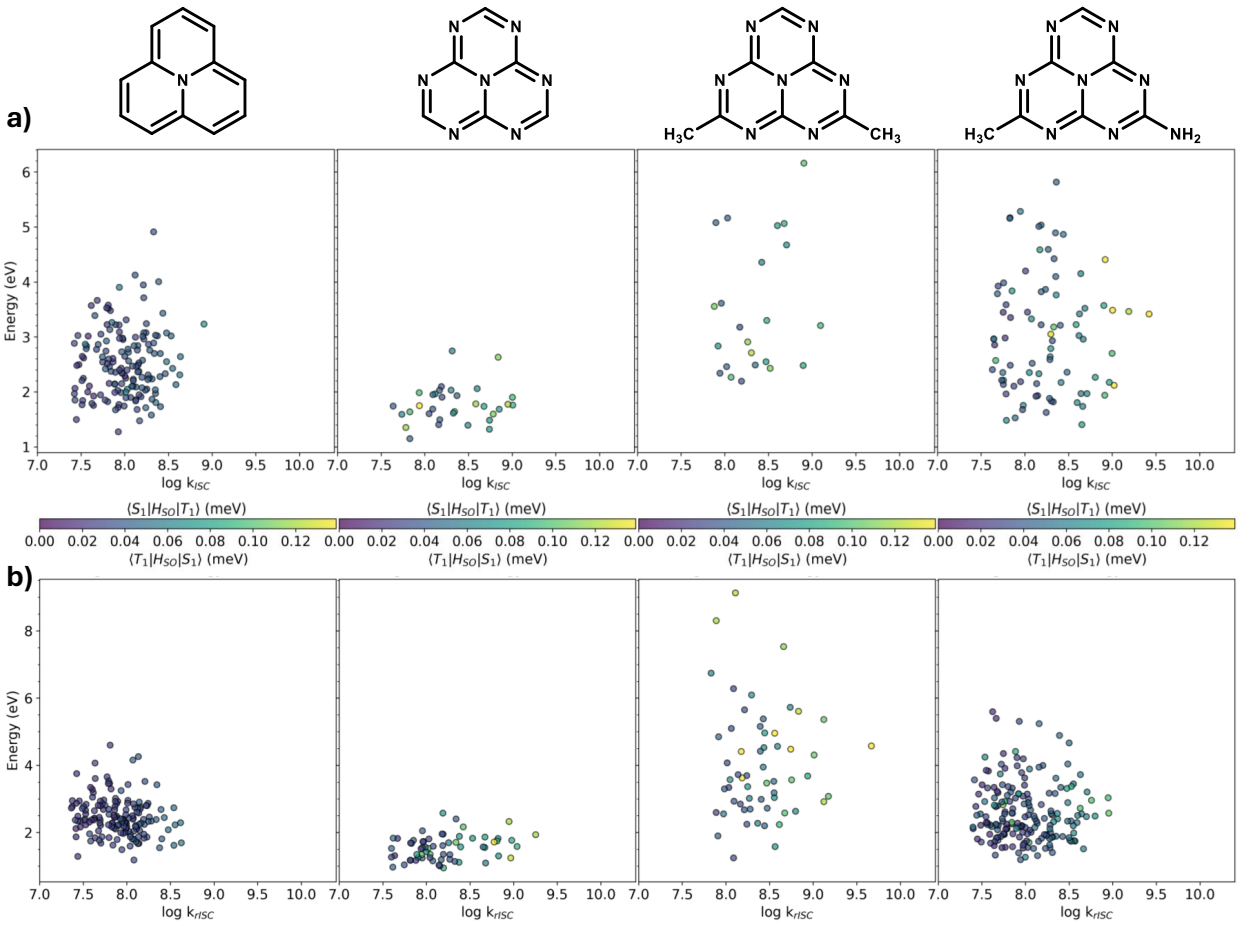

Figure S7: (a) S_1 energies relative to the minimum of S_1 PES vs. k_{ISC} vs. $\langle S_1|H_{SO}|T_1\rangle$ (color scale) and (b) T_1 energies relative to the minimum of T_1 PES vs. k_{rISC} vs vs $\langle T_1|H_{SO}|S_1\rangle$ (color scale). Only configurations contributing to the 95% of the rate constant are shown.

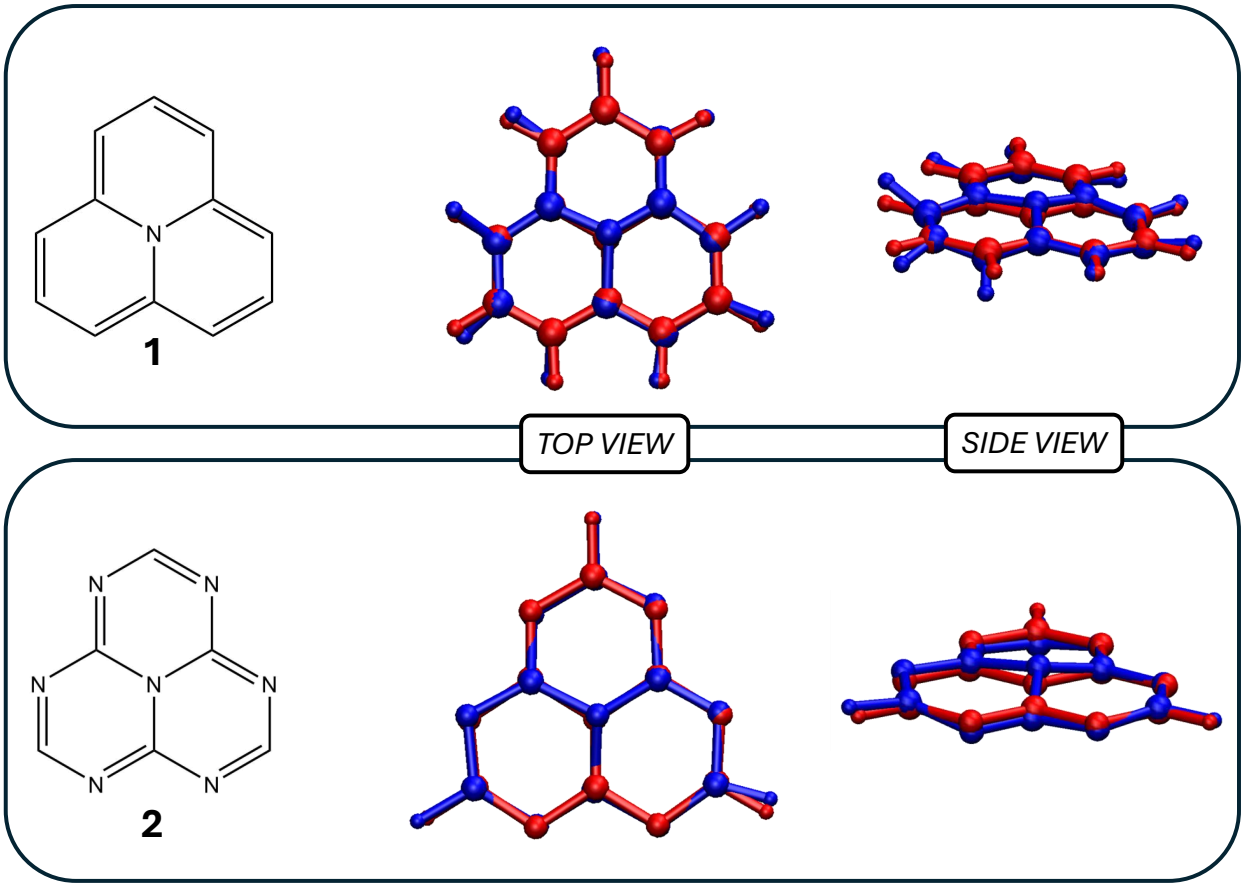

Figure S8: Top and side view of the geometries that contribute the most to k_{ISC} (blue) compared to the geometry of the optimized MECP (red) from Ref. 1.

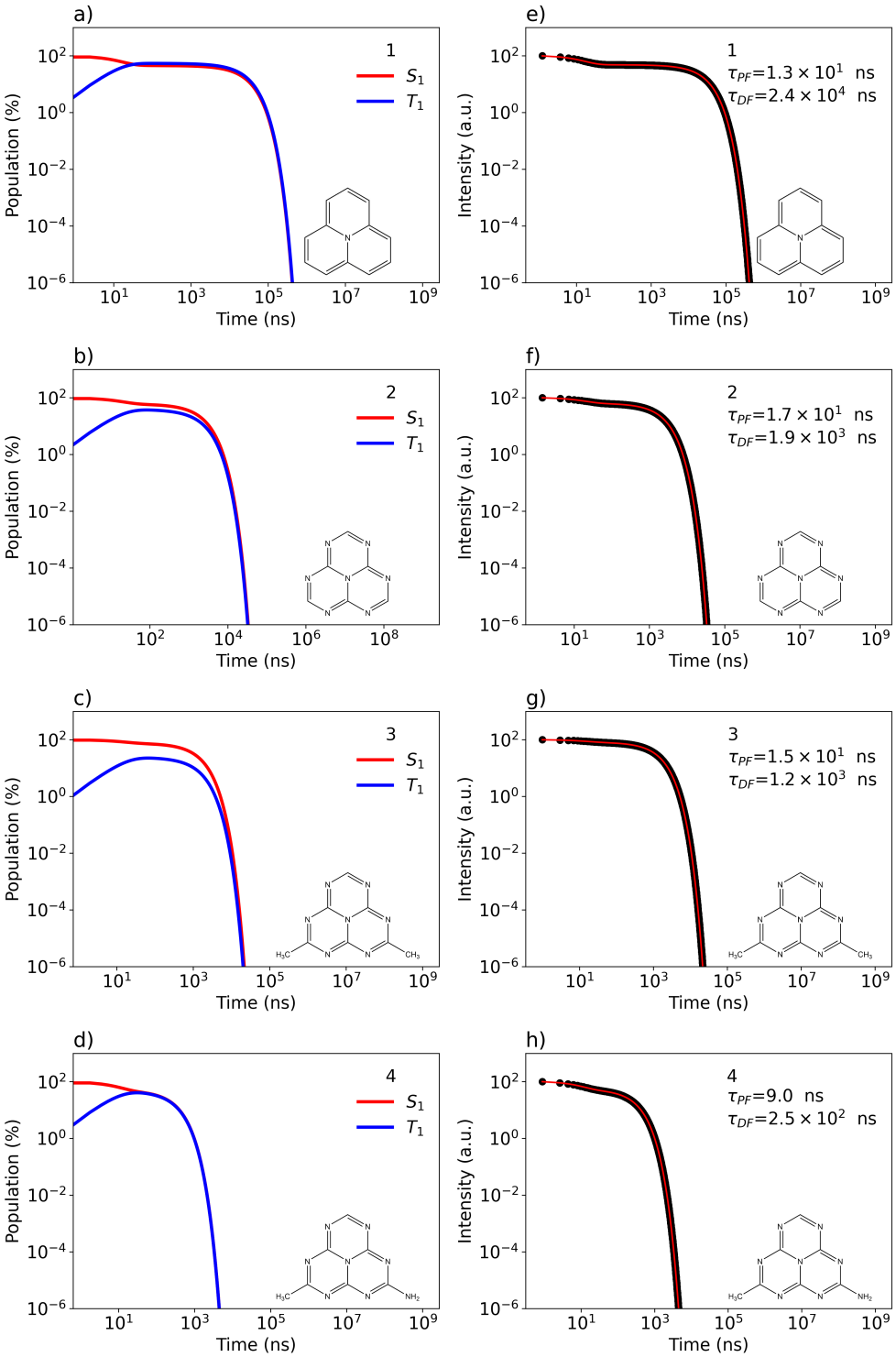

Figure S9: a-d) Time evolution of the S_1 (red) and T_1 (blue) state populations for molecules **1** to **4** under optical excitation (100% S_1 at $t = 0$) and e-h) the corresponding time-resolved photoluminescence decay (black) and its bi-exponential fit (red) for molecules **1** to **4**. (ϵ = 2.38, n_r = 1.497, EOM-CCSD/cc-pVDZ)

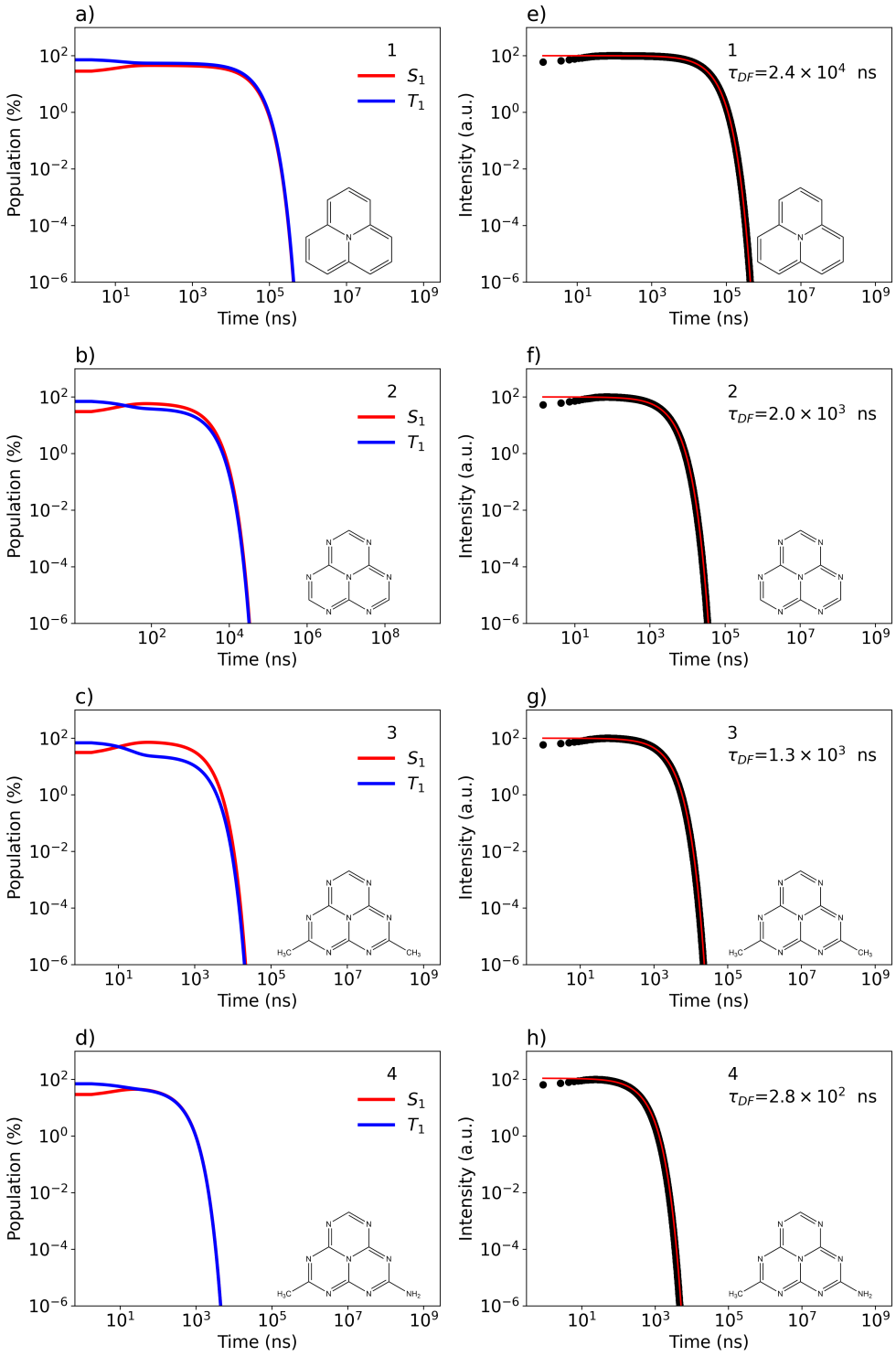

Figure S10: a-d) Time evolution of the S_1 (red) and T_1 (blue) state populations for molecules **1** to **4** under electrical excitation (25% S_1 at $t = 0$) and e-h) the corresponding time-resolved photoluminescence decay (black) and its bi-exponential fit (red) for molecules **1** to **4**. (ϵ = 2.38, n_r = 1.497, EOM-CCSD/cc-pVDZ)

References

(1) Valverde, D.; Ser, C. T.; Ricci, G.; Jorner, K.; Pollice, R.; Aspuru-Guzik, A.; Olivier, Y. Computational Investigations of the Detailed Mechanism of Reverse Intersystem Crossing in Inverted Singlet–Triplet Gap Molecules. *ACS Applied Materials & Interfaces* **2024**, *16*, 66991–67001.