Supporting Information: Toward Prediction of Nonradiative Decay Pathways in Organic Compounds I: The Case of Naphthalene Quantum Yields

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Table S1: E_{abs}, E_{fl}, and k_{fl} for family I from theory and experiments.

		E_{abs} (eV)		E_{fl} (eV)		$\log_{10}(k_{\mathrm{fl}}/\mathrm{s}^{-1})$	
#	species	theory	expt[a]	theory	expt[a]	theory[f]	expt[a]
1	NAPH	4.66	4.31	4.27	3.85	7.97	6.38
2	1MN	4.62	4.39	4.18	3.81	8.06	6.57
3	2MN	4.58	4.31	4.17	3.87	7.89	6.73
4	1HN	4.57	4.28	4.03	3.80	7.94	7.30
5	2HN	4.38	4.34	4.01	3.70	7.81	7.38
6	23DMN	4.53	4.28	4.16	3.86	7.85	6.69
7	26DMN	4.52	4.36	4.19	3.80	7.76	7.07
8	2PN	4.36	4.29	3.92	3.55	8.56	6.36
9	14DPN	4.20	4.12	3.37	3.26	8.66	8.33
10	15DPN	4.28	4.10	3.50	3.31	8.56	8.48
11	17DPN	4.20	4.17	3.42	3.40	8.38	7.18
12	ACN	4.58	4.30	4.13	3.86	8.10	7.29
$\langle\Delta_X\rangle^{b,c}$		0.19		0.27		0.98	
$\langle\lvert\Delta_X\rvert\rangle^{b,d}$		0.19		0.27		0.98	

[a] Experimental values are reported by Berlman *et al.*[S1]
[b] $\Delta_X = X_{\mathrm{theory}} - X_{\mathrm{expt}}$. $X = E_{\mathrm{abs}}$, E_{fl}, or k_{fl}.
[c] Mean signed error (MSE).
[d] Mean absolute error (MAE).
[f] Kasha emission $S_1 \rightarrow S_0$.

Table S2: E_{abs}, E_{fl}, and k_{fl} for family II from theory and experiments.

		E_{abs} (eV)		E_{fl} (eV)		$\log_{10}(k_{\mathrm{fl}}/\mathrm{s}^{-1})$	
#	species	theory	expt	theory	expt	theory[g]	expt
13	1AN[a]	4.25	3.90	3.60	3.29	7.82	7.82
14	1A4CNN[a]	4.18	3.72	3.74	3.22	8.17	8.15
15	1A4CLN[a]	4.12	3.79	3.48	3.19	7.88	7.88
16	1A4MN[a]	4.14	3.82	3.44	3.18	7.82	7.72
17	1MAN[a]	4.14	3.72	3.52	3.23	7.87	7.80
18	1DMAN[b]	4.18	4.07	3.54	3.22	7.97	7.93
19	1DMA4CNN[a]	4.00	3.69	3.57[h]	3.17	8.27[h]	8.54
20	1DMA4CLN[a]	4.06	3.89	3.44	3.14	8.03	8.03
21	1DMA4MN[a]	4.11	3.96	3.42	3.14	7.95	7.92
22	1DMA4MON[b]	4.06	3.77	3.23	3.01	7.82	7.90
23	1DMA5MON[b]	4.28	4.08	3.73	3.35	8.22	7.90
24	1DMA6MON[b]	4.11	4.09	3.50	3.22	7.95	7.86
25	1DMA7MON[b]	4.04	4.22	3.42	3.15	7.92	7.70
26	1NAZN[c]	4.15	3.80	3.55	3.17	7.99	7.89
27	1NPYN[c]	4.06	3.90	3.54[h]	3.21	8.01[h]	7.94
	$\langle\Delta_X\rangle$[d,e]	0.23		0.32		0.05	
	$\langle\lvert\Delta_X\rvert\rangle$[d,f]	0.26		0.32		0.05	

[a] Experimental values are reported by Suzuki *et al.*[S2]
[b] Experimental values are reported by Takehira *et al.*[S3]
[c] Experimental values are reported by Rückert *et al.*[S4]
[d] $\Delta_X = X_{\mathrm{theory}} - X_{\mathrm{expt}}$. $X = E_{\mathrm{abs}}$, E_{fl}, or k_{fl}.
[e] Mean signed error (MSE).
[f] Mean absolute error (MAE).
[g] Kasha emission $S_1 \rightarrow S_0$.
[h] These values are evaluated at an S_1 geometry optimized using a range-separated varient of PBE with 50% Hartree–Fock exchange in the short-range and $\omega = 0.2$ bohr^{-1} as the species collapsing into an unphysical charge-transfer excited state.

Table S3: The experimental k_{nr} is compared against the theoretical direct k_{ISC} for family I. The theoretical values of E_{ISC}, λ_{ISC}, and $E^{\ddagger}_{\mathrm{ISC}}$ are also provided.

#	Species	$\log_{10}(k_{\mathrm{nr}}/\mathrm{s}^{-1})^a$ expt^a	$\log_{10}(k_{\mathrm{ISC}}/\mathrm{s}^{-1})^b$ theory	E_{ISC} (eV) theory	λ_{ISC} (eV) theory	$E^{\ddagger}_{\mathrm{ISC}}$ (eV) theory
1	NAPH	6.90	6.92	1.41	0.26	2.71
2	1MN	7.05	7.08	1.36	0.25	2.58
3	2MN	7.06	7.36	1.39	0.26	2.63
4	1HN	7.87	7.43	1.26	0.25	2.30
5	2HN	7.71	7.86	1.29	0.26	2.32
6	23DMN	6.90	7.65	1.37	0.25	2.60
7	26DMN	7.16	7.62	1.35	0.24	2.63
8	2PN	6.81	7.12	1.17	0.29	1.83
9	14DPN	8.51	7.96	1.00	0.30	1.41
10	15DPN	8.42	7.74	1.02	0.25	1.61
11	17DPN	7.23	7.07	0.98	0.26	1.46
12	CAN	7.12	6.92	1.31	0.25	2.42

[a] Experimental values are reported by Berlman *et al.*[S1]

[b] Theoretical values in this work are predicted using Equation 5 in the main text with $B = 8.32 \times 10^6$ s^{-1} and $C = 1.66 \times 10^7$ s^{-1} cm^2, respectively.

Table S4: The experimental k_{nr} is compared against the theoretical direct k_{IC} for family II. The theoretical values of E_{fl}, λ_{IC}, and $E_{\mathrm{IC}}^{\ddagger}$ are also provided.

#	Species	$\log_{10}(k_{\mathrm{IC}}/\mathrm{s}^{-1})^{a,b,c}$ expt	$\log_{10}(k_{\mathrm{IC}}/\mathrm{s}^{-1})^{d}$ theory	${E_{\mathrm{IC}}}^{e}$ (eV) theory	λ_{IC} (eV) theory	$E_{\mathrm{IC}}^{\ddagger}$ (eV) theory
13	1AN[a]	7.92	7.39	3.61	0.37	10.80
14	1A4CNN[a]	9.21	9.07	3.46	0.26	13.20
15	1A4CLN[a]	8.25	7.54	3.47	0.36	10.21
16	1A4MN[a]	7.49	6.52	3.49	0.38	9.81
17	1MAN[a]	7.66	7.76	3.55	0.35	10.87
18	1DMAN[b]	9.93	9.13	3.59	0.40	9.97
19	1DMA4CNN[a]	11.24	10.92	3.34	0.29	11.31
20	1DMA4CLN[a]	10.24	9.39	3.46	0.39	9.53
21	1DMA4MN[a]	9.36	8.73	3.51	0.42	9.24
22	1DMA4MON[b]	8.45	8.36	3.44	0.46	8.34
23	1DMA5MON[b]	9.85	9.31	3.66	0.34	11.85
24	1DMA6MON[b]	9.85	8.26	3.49	0.37	10.16
25	1DMA7MON[b]	7.91	-	3.45	0.37	9.84
26	1NAZN[c]	8.68	9.72	3.52	0.36	10.56
27	1NPYN[c]	10.09	11.29	3.50	0.32	11.52

[a] Experimental values are reported by Suzuki *et al.*[S2]

[b] Experimental values are reported by Takehira *et al.*[S3]

[c] Experimental values are reported by Rückert *et al.*[S4]

[d] Theoretical values in this work are predicted using Equation 5 in the main text with $A_{\mathrm{IC}} = 2.02 \times 10^{12}$ s^{-1} and a slope of -8.18 eV^{-1}.

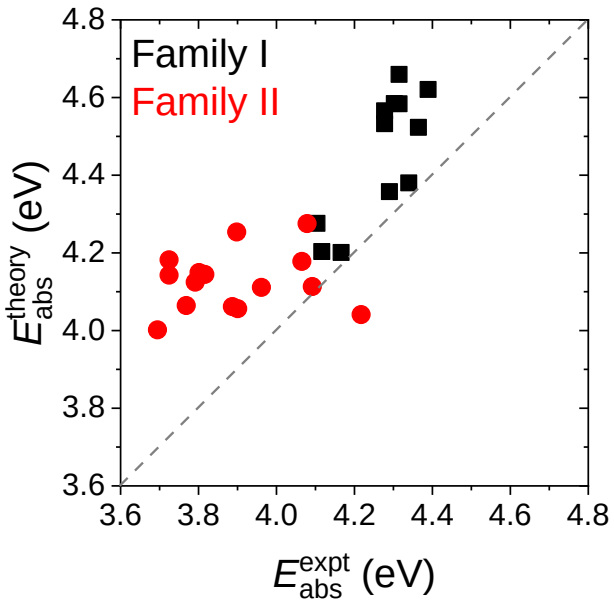

Figure S1: Comparison between the theoretical and experimental values for E_{abs} for families I (black squares) and II (red circles).

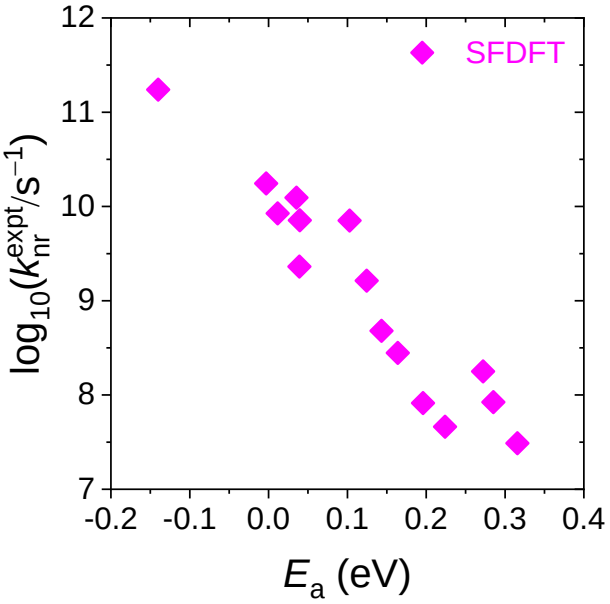

Figure S2: Energy gap law correlation between k_{nr} and E_{a} evaluated using the SFDFT/BHHLYP approach. E_{a} is treated as the difference between the FC minimum on the S_1 surface and the S_1/S_0 MECI.

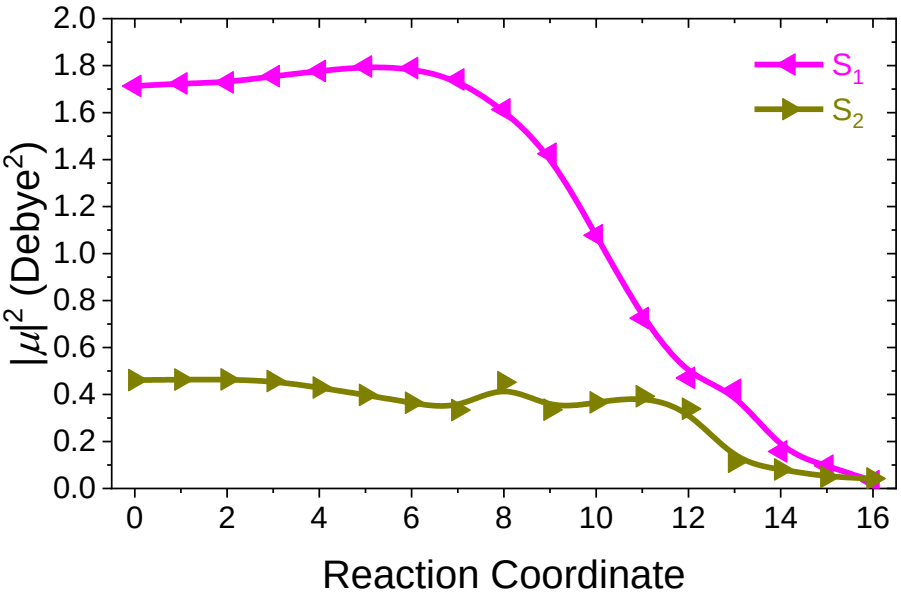

Figure S3: $|\mu|^2$'s of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions along the reaction path described in Figure 6 of the main text. S_1 and S_2 do not seem to switch in character.

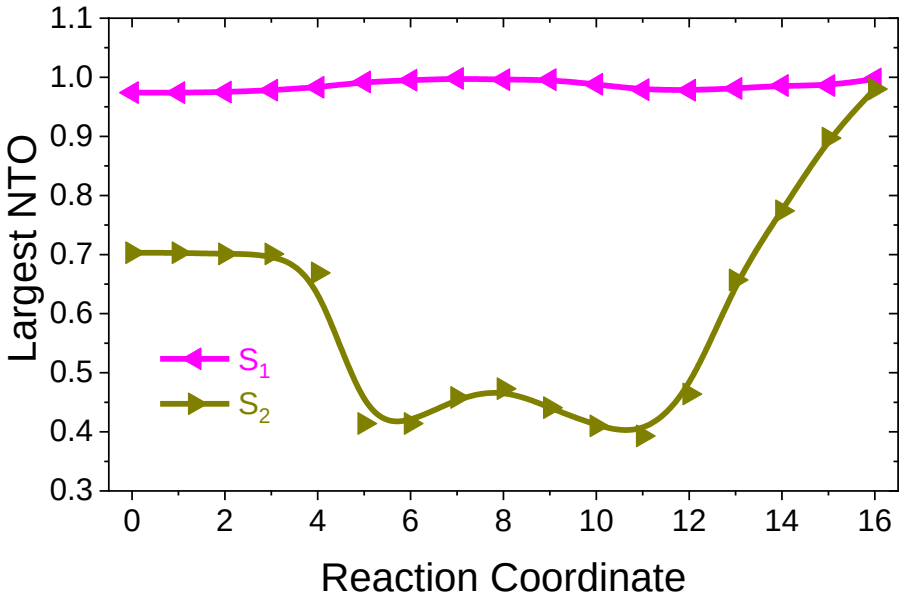

Figure S4: The percentage of the largest NTOs of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions along the reaction path described in Figure 6 of the main text. S_1 and S_2 do not seem to switch in character.

References

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