Supplementary Information for "Degenerate and Non-Degenerate Two-Photon Absorption of Coumarin Dyes"

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Contents

List of Figures

List of Tables

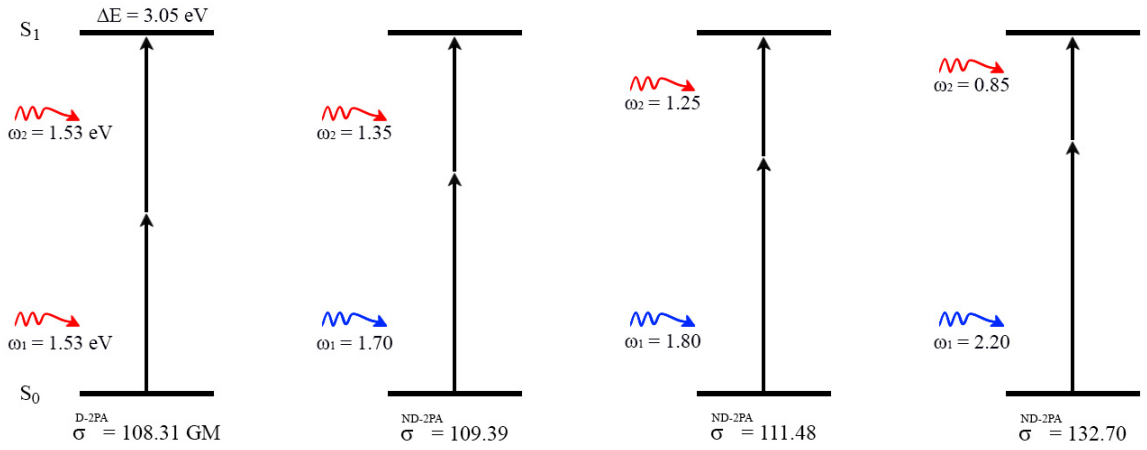

Figure S1: D-2PA and ND-2PA scan of coumarin 6 at the CAM-B3LYP/aug-cc-pVDZ level of theory in DMSO.

Table S1: The magnitudes of the transition dipole moments (μ_{01} in a.u.) for the excitation from S_0 to S_1 in MeOH, ClForm, and DMSO at the CAM-B3LYP/aug-cc-pVDZ level of theory.

Dye	MeOH	ClForm	DMSO
Coumarin	1.98	1.97	2.21
Coumarin 6	4.47	4.46	4.67
Coumarin 120	2.65	2.64	2.86
Coumarin 307	2.86	2.84	3.07
Coumarin 343	3.71	3.65	3.98

Table S2: Excitation energies (ω (eV)) and 2PA cross-sections (σ^{2PA} (GM)) for the transitions to S_1 for D-2PA and ND-2PA of **coumarin** calculated in CPCM at the CAM-B3LYP/aug-cc-pVDZ level of theory.

	D-2PA			ND-2PA								
Solvent	ω	$\frac{\omega}{2}$	σ^{2PA}	$\sigma^{2PA}_{\omega=2.5}$	$\sigma^{2PA}_{\omega=2.6}$	$\sigma^{2PA}_{\omega=2.7}$	$\sigma^{2PA}_{\omega=2.8}$	$\sigma^{2PA}_{\omega=2.9}$	$\sigma^{2PA}_{\omega=3.0}$	$\sigma^{2PA}_{\omega=3.1}$	$\sigma^{2PA}_{\omega=3.2}$	$\sigma^{2PA}_{\omega=3.3}$
MeOH	4.35	2.18	2.42	2.49	2.54	2.61	2.70	2.80	2.94	3.10	3.31	3.56
ClForm	4.33	2.17	2.49	2.58	2.63	2.71	2.80	2.92	3.06	3.24	3.46	3.74
DMSO	4.33	2.17	2.98	3.08	3.14	3.23	3.34	3.48	3.65	3.87	4.13	4.45

Table S3: Excitation energies (ω (eV)) and 2PA cross-sections (σ^{2PA} (GM)) for the transitions to S_1 for D-2PA and ND-2PA of **coumarin 6** calculated in CPCM at the CAM-B3LYP/aug-cc-pVDZ level of theory.

	D-2PA		ND-2PA						
Solvent	ω	$\frac{\omega}{2}$	σ^{2PA}	$\sigma^{2PA}_{\omega=1.7}$	$\sigma^{2PA}_{\omega=1.8}$	$\sigma^{2PA}_{\omega=1.9}$	$\sigma^{2PA}_{\omega=2.0}$	$\sigma^{2PA}_{\omega=2.1}$	$\sigma^{2PA}_{\omega=2.2}$
MeOH	3.09	1.55	94.15	94.92	96.38	98.88	102.45	107.25	113.67
ClForm	3.10	1.55	95.62	95.67	96.43	98.02	100.50	104.04	108.81
DMSO	3.05	1.53	108.31	109.39	111.48	114.40	118.81	124.75	132.70

Table S4: Excitation energies (ΔE (eV)) and 2PA cross-sections (σ^{2PA} (GM)) for the transitions to S_1 for D-2PA and ND-2PA of **coumarin 120** calculated in CPCM at the CAM-B3LYP/aug-cc-pVDZ level of theory.

	D-2PA		ND-2PA							
Solvent	ΔE	$\frac{\omega}{2}$	σ^{2PA}	$\sigma^{2PA}_{\omega=2.2}$	$\sigma^{2PA}_{\omega=2.3}$	$\sigma^{2PA}_{\omega=2.4}$	$\sigma^{2PA}_{\omega=2.5}$	$\sigma^{2PA}_{\omega=2.6}$	$\sigma^{2PA}_{\omega=2.7}$	$\sigma^{2PA}_{\omega=2.8}$
MeOH	3.98	1.99	29.22	29.57	30.01	30.65	31.50	32.59	33.97	35.70
ClForm	4.00	2.00	30.55	30.84	31.28	31.93	32.78	33.89	35.29	37.04
DMSO	3.95	1.98	34.53	34.97	35.55	36.36	37.44	38.82	40.57	42.76

Table S5: Excitation energies (ω (eV)) and 2PA cross-sections (σ^{2PA} (GM)) for the transitions to S_1 for D-2PA and ND-2PA of **coumarin 307** calculated in CPCM at the CAM-B3LYP/aug-cc-pVDZ level of theory.

	D-2PA		ND-2PA							
Solvent	ω	$\frac{\omega}{2}$	σ^{2PA}	$\sigma^{2PA}_{\omega=1.9}$	$\sigma^{2PA}_{\omega=2.0}$	$\sigma^{2PA}_{\omega=2.1}$	$\sigma^{2PA}_{\omega=2.2}$	$\sigma^{2PA}_{\omega=2.3}$	$\sigma^{2PA}_{\omega=2.4}$	$\sigma^{2PA}_{\omega=2.5}$
MeOH	3.49	1.75	64.93	65.52	66.59	68.22	70.51	73.56	77.54	82.68
ClForm	3.35	1.77	71.72	72.11	73.14	74.77	77.09	80.19	84.24	89.46
DMSO	3.46	1.73	75.55	76.47	77.84	79.91	82.77	86.57	91.52	97.93

Table S6: Excitation energies (ω (eV)) and 2PA cross-sections (σ^{2PA} (GM)) for the transitions to S_1 for D-2PA and ND-2PA of **coumarin 343** calculated in CPCM at the CAM-B3LYP/aug-cc-pVDZ level of theory.

	D-2PA		ND-2PA						
Solvent	ω	$\frac{\omega}{2}$	σ^{2PA}	$\sigma^{2PA}_{\omega=1.8}$	$\sigma^{2PA}_{\omega=1.9}$	$\sigma^{2PA}_{\omega=2.0}$	$\sigma^{2PA}_{\omega=2.1}$	$\sigma^{2PA}_{\omega=2.2}$	$\sigma^{2PA}_{\omega=2.3}$
MeOH	3.27	1.64	67.73	68.45	69.53	71.29	73.74	77.03	81.34
ClForm	3.27	1.64	81.90	82.38	83.72	85.79	88.67	92.54	97.62
DMSO	3.23	1.62	80.42	81.52	82.98	85.29	88.46	92.73	98.32

Table S7: Excitation energies (ΔE (eV)) and D-2PA cross-sections (σ^{D-2PA} (GM)) for the transitions to S_1, S_2, and S_3 in CPCM at the CAM-B3LYP/aug-cc-pVDZ level of theory.

		MeOH		ClForm		DMSO	
Dye	State	ΔE	$\sigma^{\text{D-2PA}}$	ΔE	$\sigma^{\text{D-2PA}}$	ΔE	$\sigma^{\text{D-2PA}}$
Coumarin	S_1	4.35	2.42	4.33	2.49	4.33	2.98
	S_2	4.78	4.50	4.80	5.20	4.77	5.20
	S_3	5.80	13.20	5.09	0.003	5.19	0.003
Coumarin 6	S_1	3.09	94.15	3.10	95.62	3.05	108.31
	S_2	4.33	3.80	4.33	0.10	4.32	1.40
	S_3	4.46	141.70	4.42	95.20	4.45	358.60
Coumarin 120	S_1	3.98	29.22	4.00	30.55	3.95	34.53
	S_2	4.67	10.90	4.68	14.00	4.67	13.00
	S_3	5.22	0.80	5.22	1.10	5.20	0.90
Coumarin 307	S_1	3.49	64.93	3.53	71.72	3.46	75.55
	S_2	4.42	12.6	4.45	17.00	4.42	15.3
	S_3	4.91	1.90	4.93	2.00	4.90	2.40
Coumarin 343	S_1	3.27	67.73	3.27	81.90	3.23	80.42
	S_2	4.14	23.5	4.16	33.60	4.14	29.4
	S_3	4.72	1.90	4.71	1.10	4.71	2.60

Table S8: Two-photon absorption transition moments, $\delta_{\omega}^{2\mathrm{PA}}$ (in a.u.), calculated using quadratic response theory at different ω values at the CAM-B3LYP/aug-cc-pVDZ level of theory in MeOH.

ω (eV)	Coumarin	Coumarin 6	Coumarin 120	Coumarin 307	Coumarin 343
1.6	–	9157	–	–	–
1.7	–	9308	–	–	5889
1.8	–	9618	–	4950	5994
1.9	–	10134	–	5025	6189
2.0	–	10889	–	5178	6504
2.1	–	11953	–	5416	6954
2.2	119	13452	1750	5757	7582
2.3	119	–	1800	6228	8448
2.4	121	–	1873	6868	–
2.5	125	–	1972	7740	–
2.6	129	–	2105	8945	–
2.7	136	–	2277	–	–
2.8	144	–	2503	–	–
2.9	155	–	2801	–	–
3.0	168	–	3197	–	–
3.1	186	–	–	–	–
3.2	208	–	–	–	–
3.3	238	–	–	–	–

Table S9: Two-photon absorption transition moments, $\delta_{\omega}^{2\mathrm{PA}}$ (in a.u.), calculated using quadratic response theory at different ω values at the CAM-B3LYP/aug-cc-pVDZ level of theory in ClForm.

ω (eV)	Coumarin	Coumarin 6	Coumarin 120	Coumarin 307	Coumarin 343
1.6	–	9236	–	–	–
1.7	–	9389	–	–	7091
1.8	–	9707	–	5331	7214
1.9	–	10214	–	5395	7453
2.0	–	10958	–	5538	7826
2.1	–	12006	2059	5770	8362
2.2	124	13481	1804	6105	9109
2.3	125	–	1854	6569	10139
2.4	127	–	1926	7198	–
2.5	131	–	2026	8050	–
2.6	136	–	2157	9218	–
2.7	143	–	2330	–	–
2.8	152	–	2554	–	–
2.9	163	–	2849	–	–
3.0	178	–	3241	–	–
3.1	197	–	–	–	–
3.2	222	–	–	–	–
3.3	255	–	–	–	–

Table S10: Two-photon absorption transition moments, δ_{ω}^{2PA} (in a.u.), and θ (°) calculated using quadratic response theory at different ω values at the CAM-B3LYP/aug-cc-pVDZ level of theory in DMSO.

ω (eV)	Coumarin	Coumarin 6	Coumarin 120	Coumarin 307	Coumarin 343
1.6	–	10831	–	–	–
1.7	–	11045	–	–	7184
1.8	–	11481	–	5873	7339
1.9	–	12132	–	5978	7609
2.0	–	13110	–	6177	8034
2.1	–	14489	2065	6483	8638
2.2	148	16443	2105	6919	9482
2.3	149	–	2171	7519	10651
2.4	152	–	2265	8336	–
2.5	156	–	2393	9455	–
2.6	162	–	2563	11012	–
2.7	170	–	2786	–	–
2.8	181	–	3077	–	–
2.9	195	–	3463	–	–
3.0	212	–	3981	–	–
3.1	235	–	–	–	–
3.2	264	–	–	–	–
3.3	304	–	–	–	–
θ (°)	21.60	170.62	17.76	9.75	168.03

Table S11: ND-2PA cross-sections of the 2-state model ($\sigma_\omega^{\text{ND-2SM}}$), ratio of non-degenerate to degenerate photon energies (Enh.) and ND-2PA cross-sections ($\sigma_\omega^{\text{ND-2PA}}$) computed using quadratic response of **coumarin** at the CAM-B3LYP/aug-cc-pVDZ level of theory in DMSO.

	Coumarin		
ω (eV)	$\sigma_\omega^{\text{ND-2SM}}$	$\sigma_\omega^{\text{ND-2PA}}$	Enh.
2.17[a]	4.80[a]	2.98[a]	1.00
2.2	4.80	2.99	1.00
2.3	4.80	3.00	1.00
2.4	4.84	3.03	1.01
2.5	4.90	3.08	1.02
2.6	4.99	3.14	1.04
2.7	5.14	3.23	1.07
2.8	5.22	3.34	1.09
2.9	5.42	3.48	1.13
3.0	5.61	3.65	1.17
3.1	5.90	3.87	1.23
3.2	6.24	4.13	1.30
3.3	6.63	4.45	1.38
Relative change (%)[b]	38.2	49.5	38.0

[a]D-2PA values, $\sigma^{\text{D-2PA}}$ from Eq. 3 ($N = 8$).
[b]Final σ^{ND} values relative to σ^{D}.

Table S12: ND-2PA cross-sections of the 2-state model ($\sigma_\omega^{\text{ND-2SM}}$), ratio of non-degenerate to degenerate photon energies (Enh.) and ND-2PA cross-sections ($\sigma_\omega^{\text{ND-2PA}}$) computed using quadratic response of **coumarin 120** at the CAM-B3LYP/aug-cc-pVDZ level of theory in DMSO.

	Coumarin 120		
ω (eV)	$\sigma_\omega^{\text{ND-2SM}}$	$\sigma_\omega^{\text{ND-2PA}}$	Enh.
1.98[a]	41.73[a]	34.53[a]	1.00
2.2	42.14	34.97	1.01
2.3	42.99	35.55	1.03
2.4	43.81	36.36	1.05
2.5	45.07	37.44	1.08
2.6	46.32	38.82	1.11
2.7	48.40	40.57	1.16
2.8	50.50	42.76	1.21
2.9	53.42	45.51	1.28
3.0	57.17	48.97	1.37
Relative change (%)[b]	37.0	42.0	37.0

[a]D-2PA values, $\sigma^{\text{D-2PA}}$ from Eq. 3 ($N = 8$).
[b]Final σ^{ND} values relative to σ^{D}.

Table S13: ND-2PA cross-sections of the 2-state model ($\sigma_\omega^{\text{ND-2SM}}$), ratio of non-degenerate to degenerate photon energies (Enh.) and ND-2PA cross-sections ($\sigma_\omega^{\text{ND-2PA}}$) computed using quadratic response of **coumarin 307** at the CAM-B3LYP/aug-cc-pVDZ level of theory in DMSO.

	Coumarin 307		
ω (eV)	$\sigma_\omega^{\text{ND-2SM}}$	$\sigma_\omega^{\text{ND-2PA}}$	Enh.
1.73[a]	96.95[a]	75.55[a]	1.00
1.9	97.93	76.47	1.01
2.0	98.88	77.84	1.03
2.1	101.81	79.91	1.06
2.2	104.71	82.77	1.10
2.3	108.58	86.57	1.15
2.4	114.41	91.52	1.21
2.5	121.20	97.93	1.25
Relative change (%)[b]	25.0	29.6	25.0

[a]D-2PA values, $\sigma^{\text{D-2PA}}$ from Eq. 3 ($N = 8$).
[b]Final σ^{ND} values relative to σ^{D}.

Table S14: ND-2PA cross-sections of the 2-state model ($\sigma_\omega^{\text{ND-2SM}}$), ratio of non-degenerate to degenerate photon energies (Enh.) and ND-2PA cross-sections ($\sigma_\omega^{\text{ND-2PA}}$) computed using quadratic response of **coumarin 343** at the CAM-B3LYP/aug-cc-pVDZ level of theory in DMSO.

	Coumarin 343		
ω (eV)	$\sigma_\omega^{\text{ND-2SM}}$	$\sigma_\omega^{\text{ND-2PA}}$	Enh.
1.62[a]	97.04[a]	80.42[a]	1.00
1.8	98.01	81.52	1.01
1.9	99.95	82.98	1.03
2.0	102.87	85.29	1.06
2.1	106.75	88.46	1.10
2.2	111.59	92.73	1.15
2.3	118.39	98.32	1.22
Relative change (%)[b]	22.0	22.0	22.0

[a]D-2PA values, $\sigma^{\text{D-2PA}}$ from Eq. 3 ($N = 8$).
[b]Final σ^{ND} values relative to σ^{D}.