Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Three-Photon-Induced Singlet Excited-State Absorption for the Tunable Ultrafast Optical-Limiting in Distyrylbenzene: A First-Principles Study

(Supporting Information)

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Table S1. Excitation energy ΔE, 2PA energy E_{2PA}, 2PA transition probability δ_{2PA}, 3PA energy E_{3PA} and 3PA transition probability δ_{3PA} for linear polarized light of the lowest six singlet excited states of DSB molecule in vacuum using different functionals under 6-311G(d,p) basis set.

B3LYP	ΔE		E_{2PA}		δ_{2PA}	E_{3PA}		δ_{3PA}
State	*eV*	*nm*	*eV*	*nm*	*a.u.*	*eV*	*nm*	*a.u.*
S_1	3.27	379.20	1.64	756.10	0.00	1.09	1137.61	3.60E9
S_2	3.98	311.56	1.99	623.12	2.16E5	1.33	932.33	0.00
S_3	4.31	287.70	2.16	574.07	0.00	1.44	861.11	1.51E8
S_4	4.41	281.18	2.21	561.09	2.55E2	1.47	843.54	0.00
S_5	4.48	276.79	2.24	553.57	0.00	1.49	832.21	9.22E6
S_6	4.52	274.34	2.26	548.67	3.89E3	1.51	821.19	0.00
CAM-B3LYP	ΔE		E_{2PA}		δ_{2PA}	E_{3PA}		δ_{3PA}
State	*eV*	*nm*	*eV*	*nm*	*a.u.*	*eV*	*nm*	*a.u.*
S_1	3.66	338.80	1.83	677.60	0.00	1.22	1016.39	9.10E8
S_2	4.75	261.05	2.38	521.01	0.00	1.58	784.81	2.22E7
S_3	4.75	261.05	2.38	521.01	5.39E2	1.58	784.81	0.00
S_4	5.03	246.52	2.52	492.06	0.00	1.68	738.10	6.89E6
S_5	5.04	246.03	2.52	492.06	1.09E4	1.68	738.10	0.00
S_6	5.22	237.55	2.61	475.10	3.26E5	1.74	712.64	0.00

Table S2. 2PA energy $E_{2PA}(eV)$, 2PA transition probability $\delta_{2PA}(a.u.)$, 3PA energy $E_{3PA}(eV)$ and 3PA transition probability $\delta_{3PA}(a.u.)$ for linear polarized light of the lowest six singlet excited states of molecules in vacuum at BHandHLYP/6-311G(d,p) level.

State	DSB-1		DSB		DSB+1		DSB+2		DSB+3	
	E_{2PA}	δ_{2PA}	E_{2PA}	δ_{2PA}	E_{2PA}	δ_{2PA}	E_{2PA}	δ_{2PA}	E_{2PA}	δ_{2PA}
S_1	2.17	0.00	1.82	0.00	1.66	0.00	1.58	0.00	1.53	0.00
S_2	2.59	0.00	2.39	1.21E3	2.09	9.27E2	1.91	8.18E2	1.80	7.41E2
S_3	2.60	2.09E2	2.43	0.00	2.32	9.66E5	2.19	2.10E6	2.06	0.00
S_4	2.95	6.20E2	2.55	1.94E5	2.41	0.00	2.23	0.00	2.12	3.53E6
S_5	3.06	0.00	2.56	0.00	2.42	3.26E4	2.39	0.00	2.32	0.00
S_6	3.08	1.75E4	2.59	1.22E5	2.48	0.00	2.41	0.00	2.39	0.00
State	DSB-1		DSB		DSB+1		DSB+2		DSB+3	
	E_{3PA}	δ_{3PA}	E_{3PA}	δ_{3PA}	E_{3PA}	δ_{3PA}	E_{3PA}	δ_{3PA}	E_{3PA}	δ_{3PA}
S_1	1.44	3.49E7	1.21	9.74E8	1.11	6.45E9	1.05	2.08E10	1.02	4.47E10
S_2	1.72	8.03E5	1.59	0.00	1.39	0.00	1.27	0.00	1.20	0.00
S_3	1.73	0.00	1.62	2.46E7	1.54	0.00	1.46	0.00	1.37	5.91E9
S_4	1.96	0.00	1.70	0.00	1.60	2.74E8	1.48	4.40E9	1.41	0.00
S_5	2.04	8.60E6	1.71	6.99E6	1.61	0.00	1.59	6.50E9	1.54	7.36E9
S_6	2.05	0.00	1.72	0.00	1.65	2.28E9	1.61	6.97E8	1.59	3.30E11

Table S3. Cartesian coordinates of DSB, DSB dimer and DSB trimer in S_0 state.

DSB				DSB trimer			
Atoms	X	Y	Z	Atoms	X	Y	Z
C	-6.15848	3.892108	0	C	-8.07656	-1.02069	-2.98222
C	-4.96229	3.204898	0	C	-6.68913	-1.02365	-2.94075
C	-4.93791	1.808884	0	C	-6.00317	-1.42576	-1.78033
C	-6.15848	1.135865	0	C	-6.763	-1.84234	-0.6769
C	-7.35817	1.823785	0	C	-8.15247	-1.83789	-0.71837
C	-7.36404	3.206475	0	C	-8.8177	-1.42471	-1.86933
H	-6.15285	4.968718	0	H	-8.58522	-0.70719	-3.88681
H	-4.04167	3.761115	0	H	-6.13487	-0.71765	-3.81972
H	-6.16289	0.058567	0	H	-6.25533	-2.15093	0.227396
H	-8.28662	1.278943	0	H	-8.71163	-2.15025	0.155393
H	-8.29492	3.746574	0	H	-9.90085	-1.41975	-1.90491
C	-0.00103	1.371431	0	C	-1.48459	-0.11814	-3.38734
C	1.195712	0.69022	0	C	-0.10085	-0.08751	-3.35514
C	1.227206	-0.70386	0	C	0.61436	-0.80588	-2.38105
C	0.001028	-1.37143	0	C	-0.12847	-1.56302	-1.45895
C	-1.19571	-0.69022	0	C	-1.5111	-1.59053	-1.48795
C	-1.22721	0.703859	0	C	-2.2282	-0.86418	-2.45306
H	0.007273	2.448753	0	H	-2.01265	0.441057	-4.15267
H	2.112218	1.253167	0	H	0.427961	0.493862	-4.10062
H	-0.00727	-2.44875	0	H	0.397919	-2.12845	-0.70154
H	-2.11222	-1.25317	0	H	-2.03875	-2.18404	-0.75338
C	6.158478	-1.13587	0	C	5.080119	0.959186	-3.63599
C	7.358169	-1.82379	0	C	6.47094	0.994793	-3.62404
C	7.364043	-3.20648	0	C	7.183963	0.081918	-2.8513
C	6.158478	-3.89211	0	C	6.495049	-0.85348	-2.07801
C	4.962293	-3.2049	0	C	5.108472	-0.88841	-2.08991
C	4.937914	-1.80888	0	C	4.370361	0.012495	-2.87794
H	6.162887	-0.05857	0	H	4.528417	1.666387	-4.24622
H	8.286621	-1.27894	0	H	6.995699	1.731735	-4.22116
H	8.294921	-3.74657	0	H	8.267521	0.098921	-2.84461
H	6.152849	-4.96872	0	H	7.040763	-1.55394	-1.45991
H	4.041669	-3.76112	0	H	4.596581	-1.62251	-1.48219
C	-3.70508	1.022199	0	C	-4.54579	-1.4096	-1.66388
C	-2.45717	1.490494	0	C	-3.68393	-0.8689	-2.54549
C	2.457168	-1.49049	0	C	2.068921	-0.79233	-2.26978
C	3.705084	-1.0222	0	C	2.91154	-0.00347	-2.96242
H	-3.8619	-0.04506	0	H	-4.15759	-1.85556	-0.75305
H	-2.29984	2.557648	0	H	-4.0799	-0.37358	-3.42813
H	2.299843	-2.55765	0	H	2.473455	-1.47424	-1.52794
H	3.861896	0.04506	0	H	2.497251	0.70618	-3.6736

DSB dimer				C	7.623259	-3.57976	0.478255
Atoms	X	Y	Z	C	6.281413	-3.2782	0.670534
C	-8.83481	-0.50537	-1.56268	C	5.889126	-2.02069	1.162003
C	-7.48981	-0.75592	-1.33081	C	6.890728	-1.07848	1.441047
C	-7.01965	-1.0349	-0.03576	C	8.233935	-1.38138	1.25032
C	-7.95692	-1.05998	1.009346	C	8.608361	-2.63328	0.768309
C	-9.30495	-0.80785	0.778675	H	7.904173	-4.55181	0.089269
C	-9.7519	-0.52626	-0.50995	H	5.530832	-4.01533	0.411732
H	-9.17347	-0.28838	-2.56952	H	6.608026	-0.09763	1.800324
H	-6.79638	-0.72136	-2.16162	H	8.984206	-0.63111	1.468567
H	-7.61305	-1.26917	2.016649	H	9.654155	-2.86987	0.61083
H	-10.0063	-0.82969	1.605014	C	1.080614	-3.14459	1.728037
H	-10.8008	-0.32689	-0.69509	C	-0.26588	-2.85734	1.880097
C	-2.22594	-1.38663	-1.30384	C	-0.72097	-1.52802	1.901391
C	-0.86951	-1.50754	-1.05946	C	0.240525	-0.51077	1.769861
C	-0.37909	-1.61859	0.251537	C	1.585435	-0.79644	1.622134
C	-1.32198	-1.59139	1.295375	C	2.041791	-2.12474	1.593557
C	-2.67906	-1.47826	1.050443	H	1.405663	-4.17934	1.701023
C	-3.16999	-1.37748	-0.26104	H	-0.9713	-3.67563	1.958692
H	-2.57699	-1.29292	-2.32628	H	-0.08613	0.520321	1.762978
H	-0.18131	-1.49773	-1.8952	H	2.283295	0.020863	1.50127
H	-0.96866	-1.65863	2.319175	C	-5.48901	-2.5667	2.833079
H	-3.3643	-1.44934	1.888265	C	-6.83601	-2.25368	2.989017
C	4.393315	-2.14789	-1.01135	C	-7.28693	-0.96384	2.720555
C	5.758941	-2.23144	-0.76475	C	-6.38133	0.006185	2.288631
C	6.242491	-2.10187	0.53281	C	-5.03841	-0.30485	2.135222
C	5.344531	-1.88571	1.578415	C	-4.56171	-1.59845	2.41208
C	3.980643	-1.8071	1.333122	H	-5.14135	-3.57246	3.044175
C	3.473902	-1.94095	0.030025	H	-7.53136	-3.0177	3.317525
H	4.02188	-2.24187	-2.02657	H	-8.33582	-0.71606	2.832867
H	6.448925	-2.38128	-1.5866	H	-6.72589	1.004249	2.054169
H	7.307445	-2.13857	0.725264	H	-4.3599	0.460007	1.781839
H	5.714401	-1.77007	2.591053	C	4.490413	-1.64305	1.360407
H	3.303877	-1.62402	2.158322	C	3.443063	-2.48682	1.412135
C	-5.61119	-1.25417	0.27841	C	-2.12619	-1.15299	2.012059
C	-4.58197	-1.22569	-0.58564	C	-3.15526	-1.97578	2.286628
C	1.035937	-1.73178	0.577806	H	4.321607	-0.57744	1.484936
C	2.053174	-1.85229	-0.2929	H	3.628557	-3.5545	1.330047
H	-5.40727	-1.42561	1.330684	H	-2.32225	-0.09589	1.859005
H	-4.78521	-1.05514	-1.63823	H	-2.95256	-3.02816	2.466348
H	1.256115	-1.71133	1.640723	C	-7.07432	3.5108	1.07893
H	1.83097	-1.88919	-1.35494	C	-5.69168	3.407082	1.002164
C	8.834703	0.504516	-1.56261	C	-5.08574	2.577186	0.041767

C	7.489751	0.755386	-1.33082	C	-5.92042	1.871766	-0.83832
C	7.019633	1.034791	-0.03584	C	-7.30449	1.96517	-0.75533
C	7.956909	1.059979	1.009259	C	-7.88896	2.787022	0.20468
C	9.304891	0.807531	0.778661	H	-7.52186	4.157195	1.825359
C	9.751798	0.525505	-0.50988	H	-5.0803	3.978622	1.689641
H	9.173323	0.287195	-2.56939	H	-5.46965	1.225477	-1.57858
H	6.79632	0.720736	-2.16162	H	-7.91892	1.38442	-1.43194
H	7.613077	1.269482	2.01651	H	-8.96758	2.864822	0.275392
H	10.00624	0.829457	1.604998	C	-0.4235	3.19887	1.658535
H	10.80066	0.32587	-0.69497	C	0.955042	3.0894	1.587466
C	2.225986	1.386875	-1.30405	C	1.576624	2.53206	0.456506
C	0.869551	1.507727	-1.05968	C	0.745441	2.111542	-0.59635
C	0.379116	1.61864	0.251325	C	-0.63244	2.207052	-0.52115
C	1.321982	1.591379	1.295177	C	-1.25557	2.752657	0.614149
C	2.679067	1.478325	1.050245	H	-0.87815	3.636285	2.541035
C	3.170014	1.37764	-0.26124	H	1.553292	3.450599	2.414833
H	2.577058	1.293237	-2.32649	H	1.2006	1.680824	-1.47699
H	0.181342	1.497934	-1.89542	H	-1.22471	1.850333	-1.35366
H	0.968644	1.658479	2.318978	C	6.139451	2.580031	2.386121
H	3.364289	1.449234	1.888072	C	7.528418	2.515902	2.357776
C	-4.39334	2.147928	-1.01147	C	8.188322	2.281563	1.154028
C	-5.75897	2.231414	-0.76484	C	7.444587	2.097108	-0.01199
C	-6.24246	2.102071	0.532761	C	6.058394	2.153117	0.015018
C	-5.34444	1.886197	1.578379	C	5.376148	2.407458	1.218236
C	-3.98056	1.80765	1.333051	H	5.628919	2.770199	3.32411
C	-3.47388	1.94124	0.029903	H	8.093171	2.651817	3.272798
H	-4.02195	2.241731	-2.02673	H	9.270651	2.237086	1.123126
H	-6.449	2.381037	-1.58669	H	7.945838	1.896764	-0.94959
H	-7.30741	2.138769	0.725258	H	5.509494	1.993374	-0.90416
H	-5.71427	1.770789	2.59106	C	-3.63866	2.404352	-0.08044
H	-3.30376	1.624809	2.158275	C	-2.70103	2.892922	0.752684
C	5.611204	1.25434	0.278291	C	3.021675	2.362855	0.329435
C	4.581986	1.225717	-0.58575	C	3.922804	2.524143	1.31641
C	-1.03593	1.731701	0.5776	H	-3.32596	1.801743	-0.92813
C	-2.05315	1.852617	-0.29305	H	-3.01799	3.452336	1.628563
H	5.407305	1.426085	1.33052	H	3.361572	2.059823	-0.65669
H	4.785256	1.054785	-1.63827	H	3.563795	2.779856	2.309595
H	-1.25612	1.710772	1.6405				
H	-1.83094	1.88992	-1.35509				