Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Ultrafast Studies of Some Diaryl Carbenes

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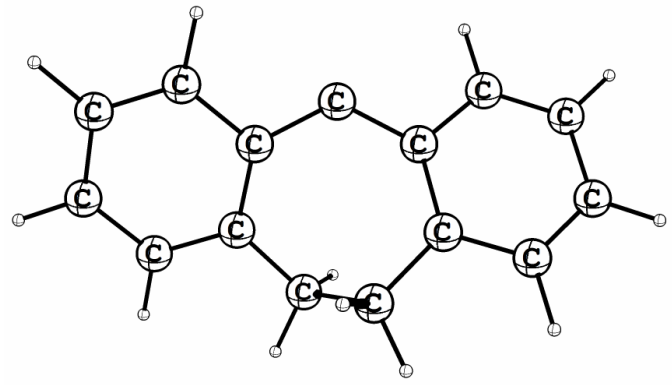
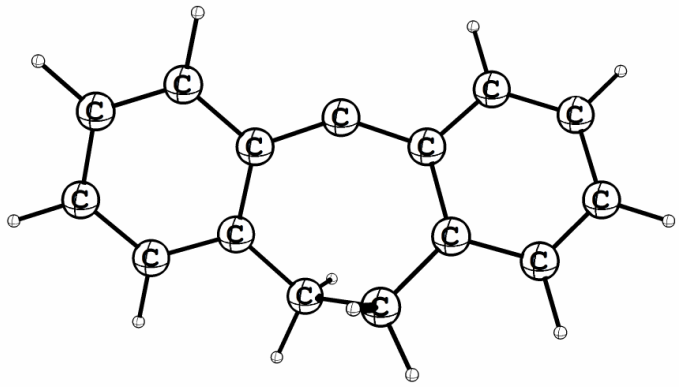


E = -578.860935925 Hartree

λ_{max}	f	λ_{max}	f	Cartesian Coordinates			
				C	-0.546437	1.720482	0.541907
1679.89	0.0047	259.88	0.0084	C	0.546413	1.720584	-0.541637
				C	1.614793	0.683587	-0.292085
				C	1.285852	-0.676437	0.015988
374.73	0.0025	259.52	0.0315	C	-0.000018	-1.342430	0.000205
				C	-1.285832	-0.676465	-0.015842
				C	-1.614828	0.683575	0.292090
371.40	0.0021	253.39	0.0117	C	-2.364194	-1.559544	-0.298511
				C	-3.690481	-1.147173	-0.304210
				C	-3.985669	0.173564	0.039055
360.34	0.0018	250.60	0.0255	C	-2.955365	1.068897	0.341482
				C	2.955332	1.068899	-0.341664
				C	3.985667	0.173564	-0.039357
359.11	0.0380	240.78	0.0066	C	3.690530	-1.147157	0.304024
				C	2.364234	-1.559513	0.298564
				H	-0.076688	1.562985	1.523898
				H	-1.018380	2.708908	0.581579
341.94	0.0335	238.08	0.0039	H	1.018370	2.709008	-0.581101
				H	0.076627	1.563287	-1.523644
				H	-2.092786	-2.590241	-0.503309
324.48	0.4712	234.94	0.0029	H	-4.487467	-1.846861	-0.540024
				H	-5.018017	0.513581	0.071226
				H	-3.203034	2.098096	0.593071
295.14	0.0011	226.23	0.0019	H	3.202983	2.098086	-0.593321
				H	5.018015	0.513568	-0.071699
				H	4.487552	-1.846828	0.539766
278.23	0.0185	225.06	0.0030	H	2.092851	-2.590189	0.503514
270.81	0.0334	223.20	0.0256				

Table S1. TD-B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations of singlet DBC and its Cartesian coordinates

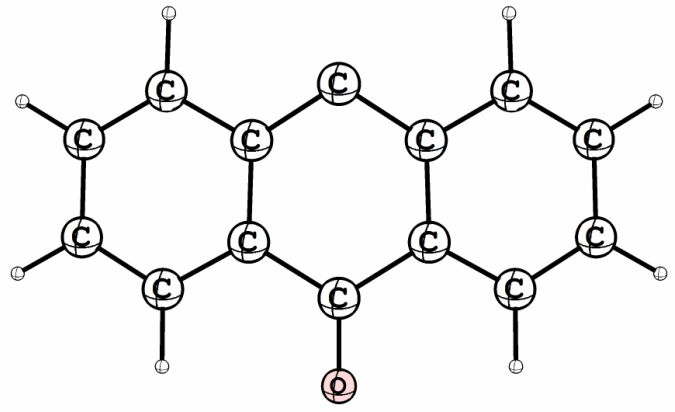


E = -578.875296183 Hartree

λ_{max}	f	λ_{max}	f
438.01	0.0077	297.53	0.0139
399.11	0.0001	289.17	0.0000
395.56	0.0042	288.8	0.0021
352.63	0.0069	279.72	0.0001
352.30	0.0523	277.49	0.001
345.17	0.0224	273.95	0.0288
323.53	0.0021	272.76	0.0009
323.34	0.5225	257.07	0.0028
320.69	0.0024	256.16	0.0157
316.8	0.0009	255.39	0.0034

Cartesian Coordinates			
C	0.582219	1.721959	-0.512910
C	-0.582190	1.721858	0.513156
C	-1.663063	0.699586	0.246312
C	-1.329388	-0.673673	-0.000279
C	-0.000027	-1.126683	-0.000129
C	1.329387	-0.673638	0.000255
C	1.663079	0.699585	-0.246392
C	2.385523	-1.599443	0.229227
C	3.711272	-1.194288	0.222543
C	4.029537	0.148703	-0.009029
C	3.004818	1.073851	-0.236149
C	-3.004786	1.073896	0.235984
C	-4.029525	0.148758	0.008896
C	-3.711299	-1.194272	-0.222485
C	-2.385563	-1.599469	-0.229112
H	0.161229	1.570067	-1.517423
H	1.042963	2.716372	-0.521274
H	-1.042866	2.716300	0.521805
H	-0.161253	1.569643	1.517644
H	2.127906	-2.638713	0.411364
H	4.499821	-1.920439	0.401052
H	5.065616	0.475438	-0.011566
H	3.257487	2.117275	-0.413609
H	-3.257427	2.117334	0.413396
H	-5.065594	0.475528	0.011353
H	-4.499871	-1.920420	-0.400907
H	-2.127977	-2.638763	-0.411155

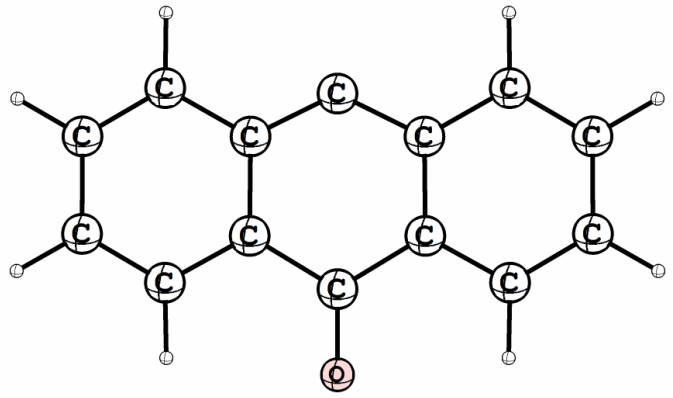
Table S2. TD-B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations of triplet DBC and its Cartesian coordinates



E = -613.587596881 Hartree

λ_{max}	f	λ_{max}	f	Cartesian Coordinates			
1581.22	0.0024	257.57	0.3551	C	-1.220926	-0.911958	0.076791
				C	-1.267712	0.511768	0.049152
				C	0.000000	1.294821	0.077572
493.2	0.0017	253.12	0.1231	C	1.267711	0.511768	0.049148
				C	1.220926	-0.911960	0.076786
459.29	0.0029	247.12	0.0067	C	0.000000	-1.664175	0.281399
				C	-2.438574	-1.619380	-0.013023
433.79	0.0373	245.84	0.0056	C	-3.651887	-0.947556	-0.142554
				C	-3.677093	0.451450	-0.123772
382.34	0.1331	244.12	0.2308	C	-2.489278	1.179764	-0.014149
				C	2.489277	1.179764	-0.014143
367.16	0.0312	237.47	0.0213	C	3.677092	0.451450	-0.123766
				C	3.651886	-0.947556	-0.142557
335.68	0.0343	237.4	0.0117	C	2.438574	-1.619381	-0.013032
				O	0.000001	2.522763	0.075892
308.09	0.0007	229.04	0.0004	H	-2.393370	-2.703512	0.027189
				H	-4.580197	-1.505989	-0.225232
289.37	0.0055	227.19	0.0169	H	-4.626458	0.976764	-0.186833
				H	-2.494301	2.265222	0.009750
282.83	0.0707	223.87	0.0034	H	2.494302	2.265222	0.009758
				H	4.626458	0.976764	-0.186821
				H	4.580197	-1.505988	-0.225237
				H	2.393371	-2.703513	0.027175

Table S3. TD-B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations of singlet AN and its Cartesian coordinates

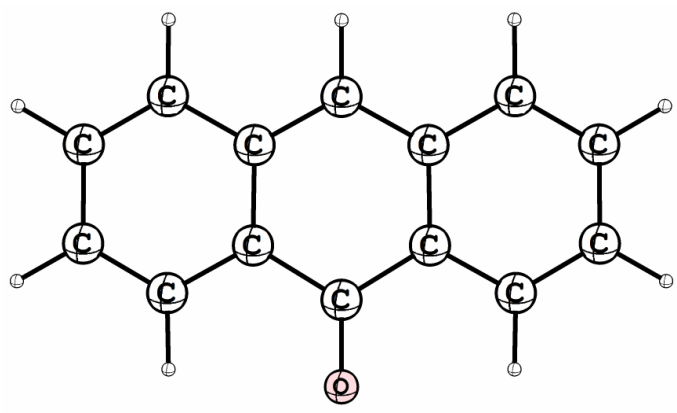


E = -613.601805465 Hartree

λ_{max}	f	λ_{max}	f
598.82	0.0000	339.33	0.0000
517.86	0.0031	337.74	0.0049
468.91	0.0063	331.42	0.0000
414.66	0.0414	307.22	0.0232
413.41	0.0243	306.50	0.0310
396.36	0.0000	299.93	0.0000
384.11	0.0000	295.82	0.0010
366.27	0.0000	285.70	0.0003
352.80	0.0000	283.43	0.0003
343.71	0.1723	266.57	0.0039

Cartesian Coordinates			
C	-1.257125	-0.935665	-0.000055
C	-1.269528	0.498315	-0.000037
C	0.000001	1.266950	-0.000096
C	1.269529	0.498314	-0.000033
C	1.257124	-0.935662	-0.000061
C	-0.000001	-1.555757	-0.000197
C	-2.490428	-1.635509	0.000006
C	-3.686255	-0.938316	0.000094
C	-3.693166	0.469109	0.000116
C	-2.494757	1.174319	0.000041
C	2.494759	1.174317	0.000056
C	3.693166	0.469106	0.000126
C	3.686253	-0.938316	0.000083
C	2.490427	-1.635508	-0.000008
O	0.000001	2.502987	-0.000122
H	-2.478936	-2.721281	-0.000020
H	-4.626877	-1.482278	0.000147
H	-4.638186	1.004789	0.000196
H	-2.474766	2.259736	0.000051
H	2.474770	2.259735	0.000082
H	4.638186	1.004786	0.000217
H	4.626874	-1.482281	0.000125
H	2.478934	-2.721280	-0.000047

Table S4. TD-B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations of triplet AN and its Cartesian coordinates

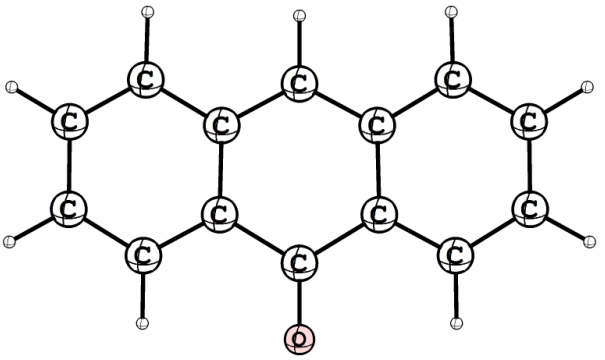


E = -614.288170904 Hartree

λ_{max}	f	λ_{max}	f
643.79	0.0000	307.99	0.0264
526.89	0.0011	305.56	0.0000
500.89	0.0135	286.29	0.0006
436.84	0.0369	269.37	0.0009
430.38	0.0416	265.28	0.0003
344.50	0.0010	259.18	0.0000
343.77	0.1410	256.29	0.0176
337.28	0.0243	254.63	0.4719
334.21	0.0000	249.89	0.0012
314.86	0.0226	247.93	0.0000

Cartesian Coordinates			
C	-1.240609	-0.902048	-0.000110
C	-1.262874	0.525198	-0.000077
C	0.000000	1.298817	-0.000106
C	1.262874	0.525198	-0.000077
C	1.240609	-0.902048	-0.000110
C	0.000000	-1.589215	-0.000278
C	-2.476866	-1.598808	0.000027
C	-3.676713	-0.909528	0.000180
C	-3.686687	0.497872	0.000165
C	-2.487905	1.202423	0.000030
C	2.487905	1.202423	0.000030
C	3.686687	0.497872	0.000165
C	3.676713	-0.909528	0.000180
C	2.476866	-1.598808	0.000027
O	0.000000	2.535444	-0.000113
H	-2.467478	-2.686086	0.000029
H	-4.615359	-1.457016	0.000301
H	-4.632310	1.032643	0.000238
H	-2.468409	2.287589	0.000001
H	2.468409	2.287589	0.000001
H	4.632310	1.032643	0.000238
H	4.615359	-1.457016	0.000301
H	2.467478	-2.686086	0.000029
H	0.000000	-2.676735	-0.000517

Table S5. TD-B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations of radical ANH· and its Cartesian coordinates



E = -614.031287028 Hartree

λ_{max}	f	λ_{max}	f
657.21	0.0000	243.00	0.0002
513.64	0.0208	241.04	0.4188
452.22	0.0325	230.77	0.0002
428.04	0.3215	226.26	0.0001
300.64	0.0000	224.75	0.0078
290.54	0.0371	219.73	0.0023
279.36	0.0000	215.56	0.0249
265.19	0.0000	213.72	0.0002
255.64	0.0000	207.36	0.3707
255.26	0.2509	206.08	0.0421

Cartesian Coordinates			
C	1.243636	-0.879941	0.000024
C	1.277641	0.548251	0.000018
C	0.000000	1.327974	0.000008
C	-1.277641	0.548251	0.000018
C	-1.243636	-0.879941	0.000024
C	0.000000	-1.546790	0.000065
C	2.458254	-1.611441	-0.000014
C	3.673970	-0.939145	-0.000061
C	3.691616	0.461168	-0.000019
C	2.496804	1.204457	0.000026
C	-2.496804	1.204457	0.000026
C	-3.691616	0.461168	-0.000019
C	-3.673970	-0.939145	-0.000061
C	-2.458254	-1.611441	-0.000014
O	0.000000	2.548037	-0.000026
H	2.428399	-2.697463	-0.000017
H	4.605518	-1.495293	-0.000120
H	4.642800	0.985338	-0.000025
H	2.513449	2.289498	0.000063
H	-2.513449	2.289498	0.000063
H	-4.642800	0.985338	-0.000025
H	-4.605518	-1.495293	-0.000120
H	-2.428399	-2.697463	-0.000017
H	0.000000	-2.635744	0.000266

Table S6. TD-B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations of ANH^+ and its Cartesian coordinates

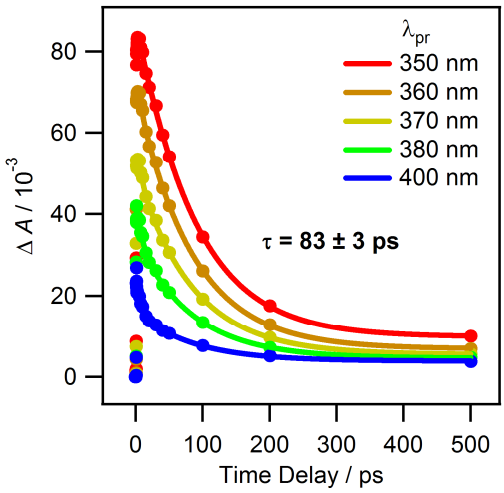


Figure S1. Kinetic traces were produced by ultrafast LFP (λ_{ex} = 308 nm) of DDBC in acetonitrile. The kinetic traces were probed at 350, 360, 370, 380 and 400 nm, respectively and globally fitted in equation $\Delta OD = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3$, where τ_1 is unlinked and τ_2 is linked. The value 83 ± 3 ps shown above is the common time constant τ_2, which is assigned to the lifetime of ^{1}DBC in acetonitrile.

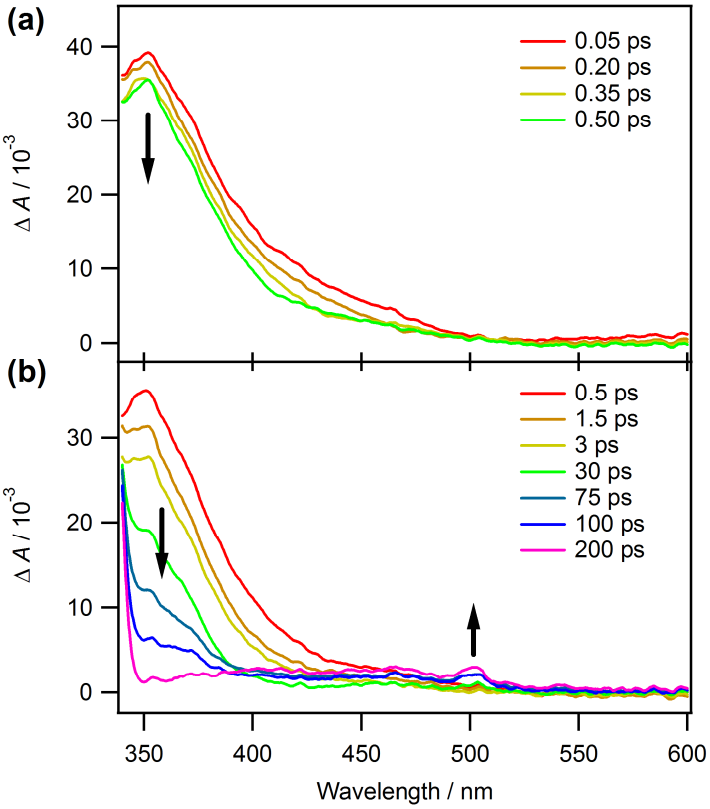


Figure S2. The transient spectra were generated by ultrafast LFP (308 nm) of DDBC in cyclohexane with time windows (a) 2–30 ps, (b) 40–200 ps and (c) 500–2500 ps.

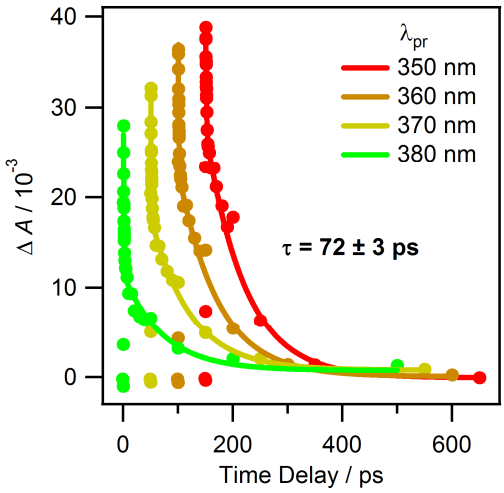


Figure S3. Kinetic traces were produced by ultrafast LFP (λ_{ex} = 308 nm) of DDBC in cyclohexane. The kinetic traces were probed at 350, 360, 370 and 380, respectively and globally fitted to the equation $\Delta OD = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3$, where τ_1 is unlinked and τ_2 is linked. The value 72 ± 3 ps shown in the figure is the common time constant τ_2, which is assigned to the lifetime of ^{1}DBC in cyclohexane. The kinetic traces are separated by 50 ps for clarity.

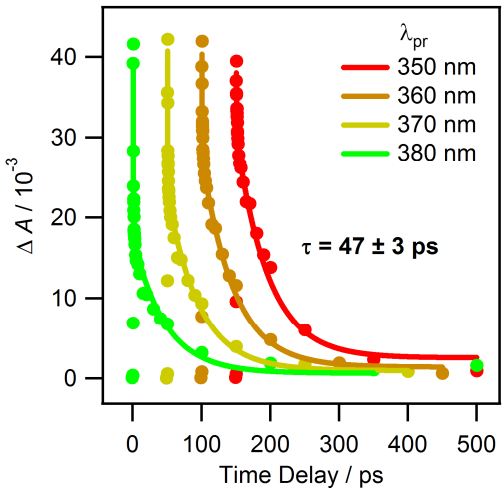


Figure S4. Kinetic traces were produced by ultrafast LFP (λ_{ex} = 308 nm) of DDBC in cyclohexene. The kinetic traces were probed at 350, 360, 370 and 380, respectively and globally fitted to the equation $\Delta OD = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3$, where τ_1 is unlinked and τ_2 is linked. The value 47 ± 3 ps shown in the figure is the common time constant τ_2, which is assigned to the lifetime of ^{1}DBC in cyclohexene. The kinetic traces are separated by 50 ps for clarity.

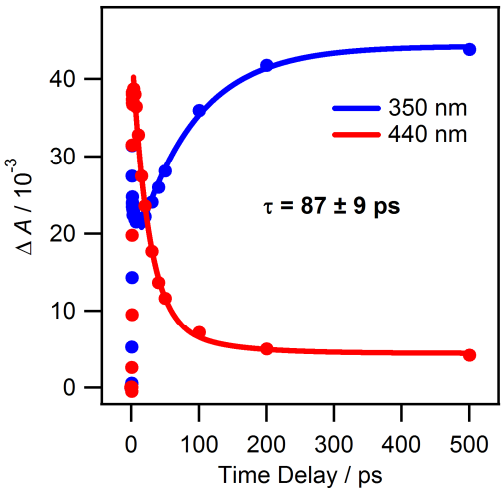


Figure S5. Kinetic traces were produced by ultrafast LFP (λ_{ex} = 308 nm) of DAN in acetonitrile. The kinetic traces were probed at 350 and 440, respectively and globally fitted to the equations $\Delta OD = A_1 \exp(-t/\tau_1) + A_2$ and $\Delta OD = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3$, where τ_1 is linked. The value 87 ± 9 ps shown above is the common time constant τ_1, which is assigned to the lifetime of ^{1}AN in acetonitrile. τ_2 is 24 ± 3 ps, which is assigned to the vibrational cooling of ^{1}AN.

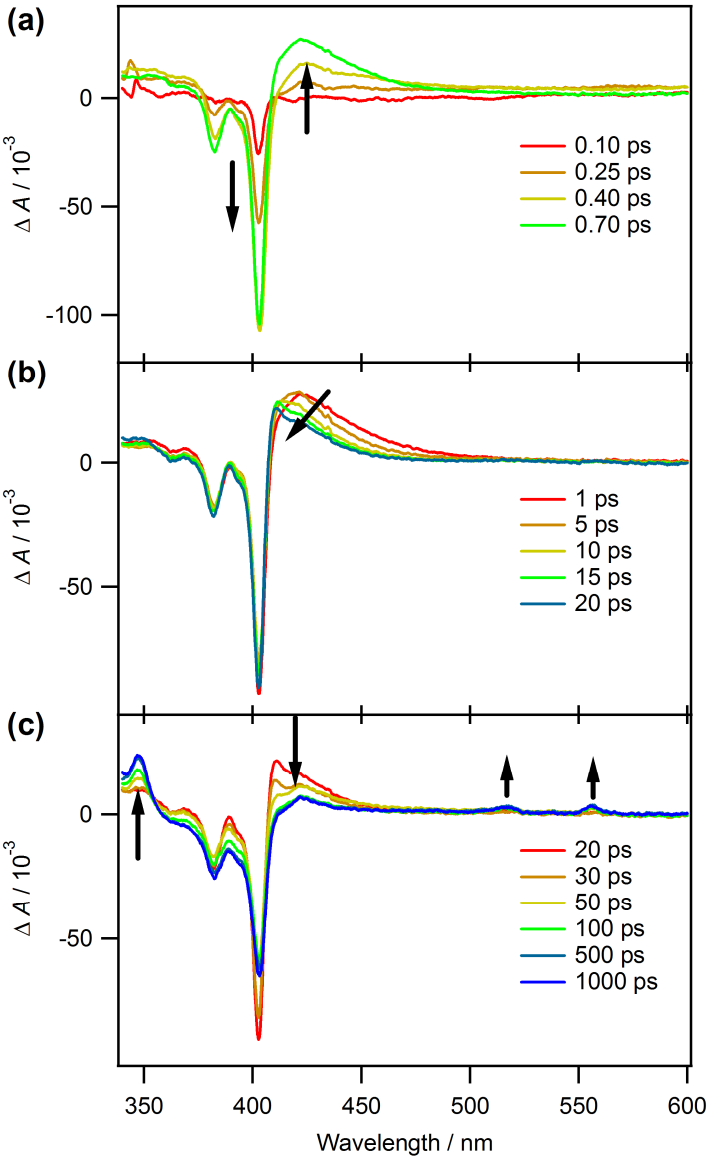


Figure S6. Transient spectra were generated by ultrafast LFP (λ_{ex} = 308 nm) of DAN in cyclohexane with time windows of (a) 0.10–0.70 ps, (b) 1–20 ps and (c) 20–1000 ps.

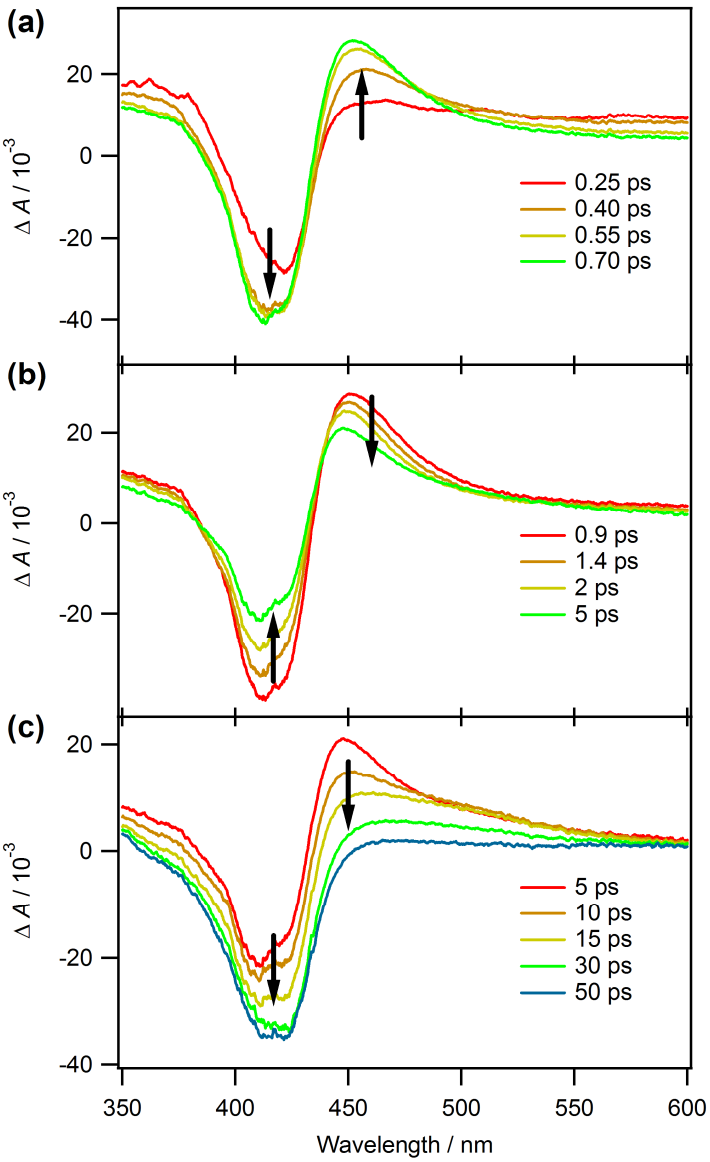


Figure S7. Transient spectra were generated by ultrafast LFP (λ_{ex} = 308 nm) of DAN in methanol with time windows of (a) 0.25–0.70 ps, (b) 0.9–5 ps and (c) 5–50 ps.

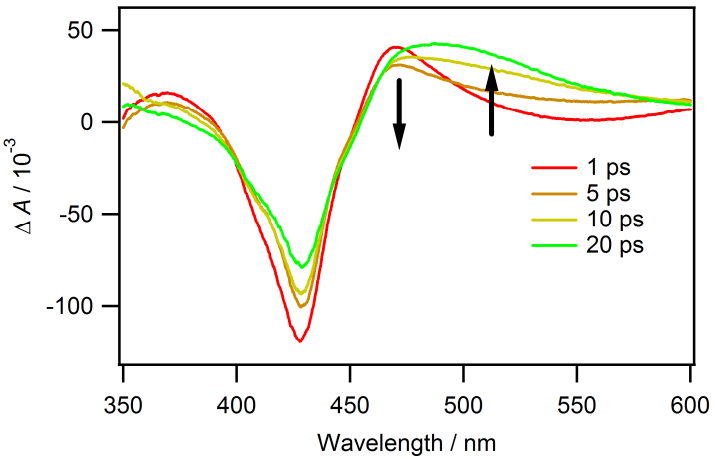


Figure S8. Transient spectra were generated by ultrafast LFP (λ_{ex} = 308 nm) of DAN in 2,2,2-trifluoroethanol with a time window of 1–20 ps.