Long lasting sunscreen controversy on 4-aminobenzoic acid and 4-dimethylaminobenzaldehyde derivatives resolved by ultrafast spectroscopy combined with density functional theoretical study

Supporting Information

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Table S1 Calculated transition energies (in nm) and the corresponding oscillation strengths (in parentheses), and major frontier orbital involved for absorption from the S_0 and fluorescence from the LE state of PABA in acetonitrile (CH_3CN) and water (H_2O) with the non-specific solute-solvent interaction.

	S_0	**LE**
PABA-S (CH_3CN)	283(0.55) H→L(97%)	313(0.79) H←L(98%)
PABA-S (H_2O)	283(0.55) H→L(97%)	314(0.80) H←L(98%)

H: HOMO; L: LUMO

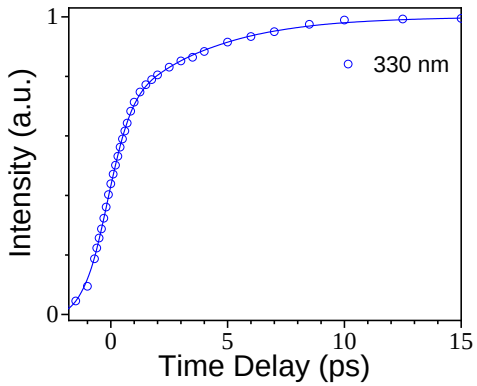

Figure S1 Early time experimental and fitted (—) decay profile of the fs-TRF at 330 nm (○) of PABA in CH_3CN.

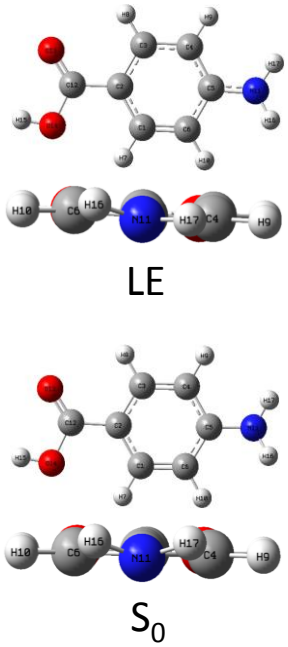

Figure S2 Optimized structures obtained from (TD)DFT calculations for the S_0 state and the LE state of PABA in CH_3CN.

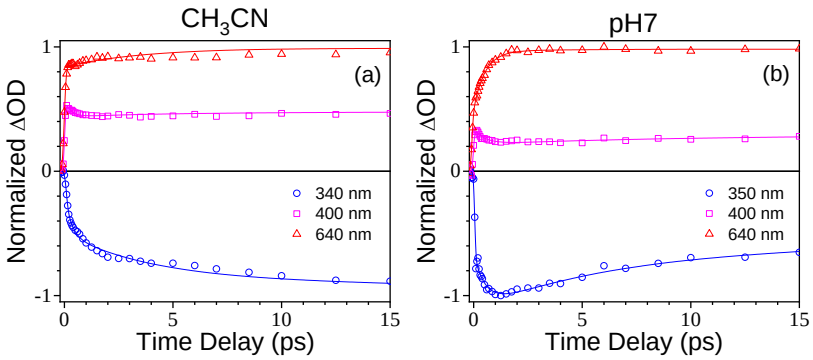

Figure S3 Experimental and fitted (—) decay profile at indicated wavelengths of the fs-TA for PABA in (a) acetonitrile and (b) pH7 buffer at early time delay up to ~15 ps.

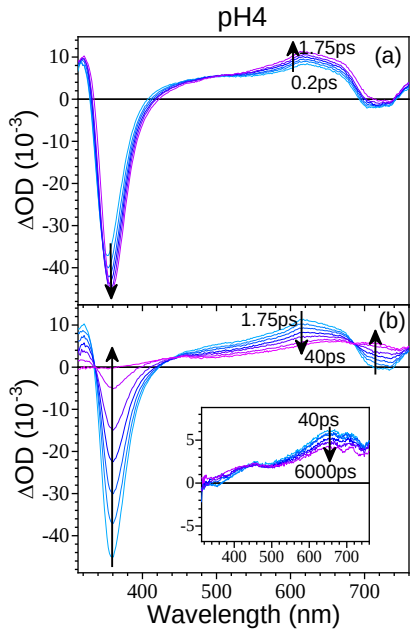

Figure S4 Temporal evolution of broadband fs-TA of PABA recorded at (a) 0.2-1.75 ps (0.2, 0.3, 0.4, 0.5, 0.7, 1.75 ps) and (b) 1.75-40 ps (1.75, 3.5, 5, 7, 10, 17.5, 40 ps) in pH4 buffer after photo-excitation. The inset in (b) shows the spectral evolution at 40-6000 ps (40, 85, 175, 1500, 2500, 6000 ps). The arrows indicate temporal evolution of the spectra.

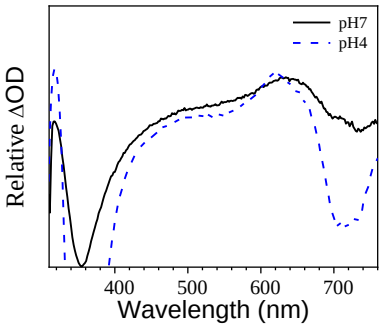

Figure S5 Comparison of the normalized fs-TA spectra of PABA in pH7 buffer at 2 ps and in pH4 buffer at 0.5 ps.

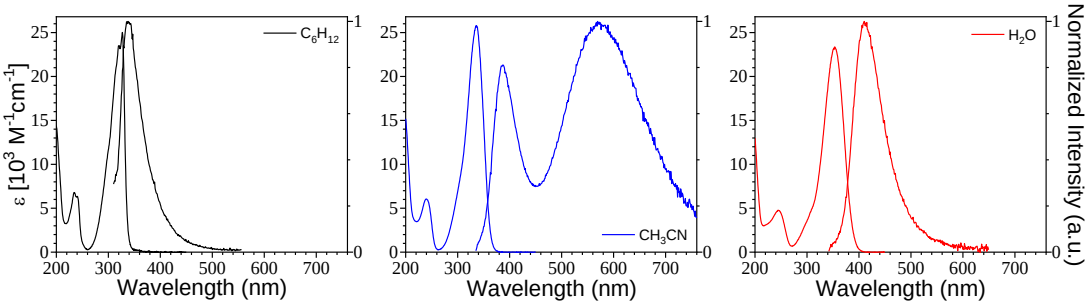

Figure S6 Steady state absorption and normalized fluorescence spectra of DMAAP in cyclohexane (black), acetonitrile (blue) and water (red).

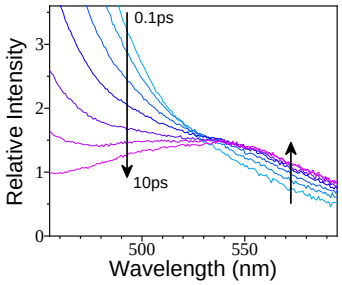

Figure S7 Magnified view of the temporal evolution of broadband fs-TRF of DMAAP recorded at 0.1-10 ps (0.1, 0.7, 1.5, 2.5, 4, 6, 10 ps) in CH_3CN after photo-excitation.

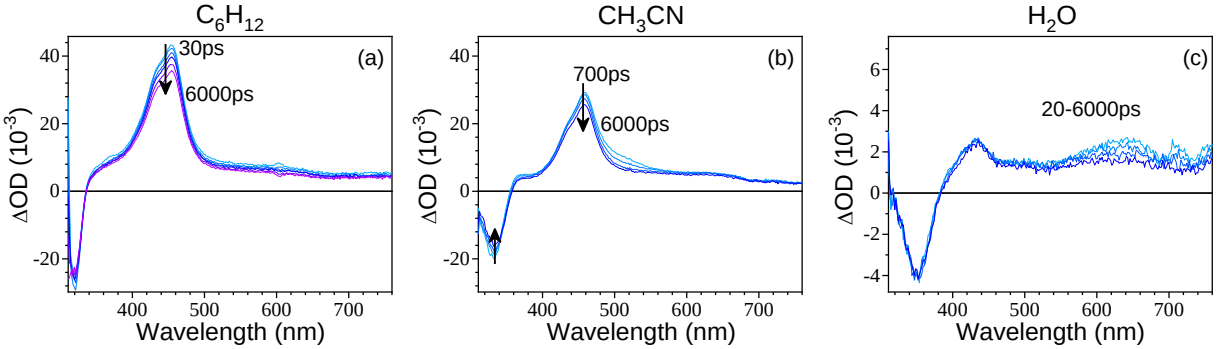

Figure S8 Temporal evolution of broadband fs-TA of DMAAP recorded at (a) 30-6000 ps (30, 350, 1250, 2500, 4000, 6000 ps) in cyclohexane; (b) 700-6000 ps (700, 1250, 2500, 6000 ps) in acetonitrile; (c) 20-6000 ps (20, 500, 2000, 6000 ps) in water after photo-excitation.

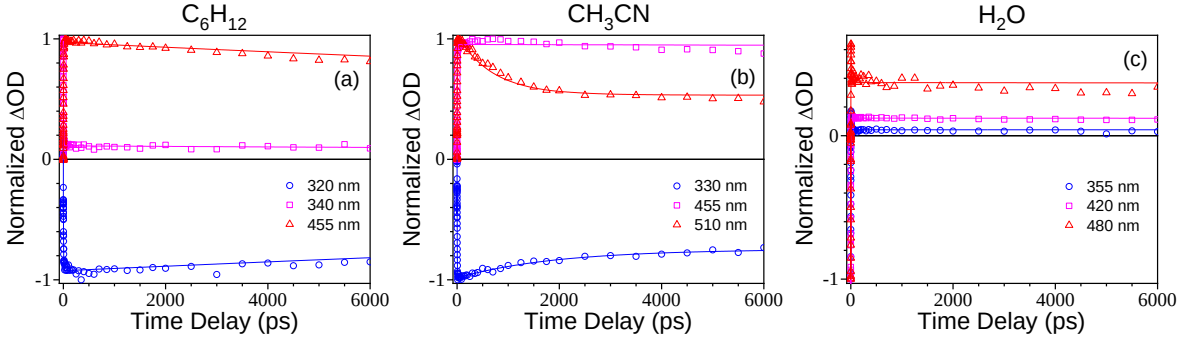

Figure S9 Experimental and fitted (—) decay profile at indicated wavelengths of the fs-TA for DMAAP in (a) cyclohexane, (b) acetonitrile and (c) water at late time delay up to ~6000 ps.

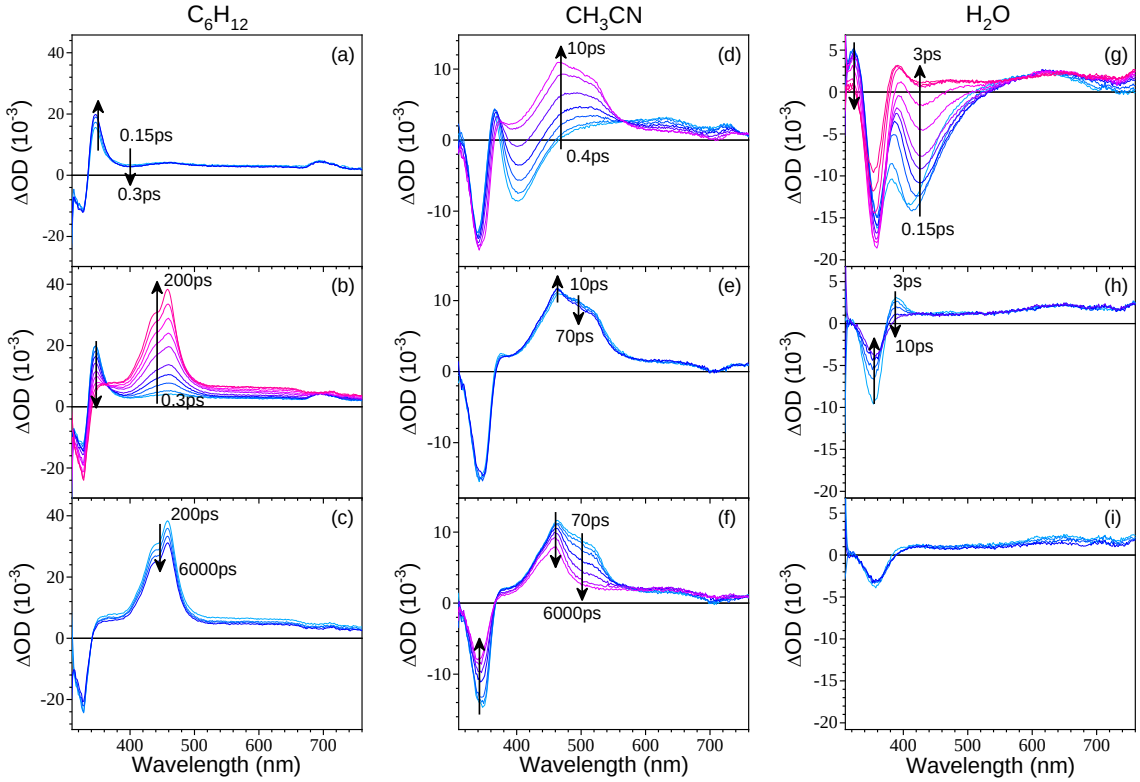

Figure S10 Temporal evolution of broadband fs-TA of DMABA recorded at (a) 0.15-0.3 ps (0.15, 0.2, 0.25, 0.3 ps), (b) 0.3-200 ps (0.3, 0.6, 1.25, 2, 3, 5, 7, 10, 15, 200 ps) and (c) 200-6000 ps (200, 1500, 3500, 6000 ps) in cyclohexane; at (d) 0.4-10 ps (0.4, 0.6, 1, 1.5, 2.5, 5, 10 ps), (e) 10-70 ps (10, 15, 40, 70 ps) and (f) 70-6000 ps (70, 100, 175, 350, 600, 1500, 6000 ps) in acetonitrile; at (g) 0.15-3 ps (0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.85, 1.25, 2, 2.5, 3 ps), (h) 3-10 ps (3, 4, 5, 7, 10 ps) and (i) 10-6000 ps (10, 200, 1250, 6000 ps) in water after photo-excitation. The arrows indicate temporal evolution of the spectra.

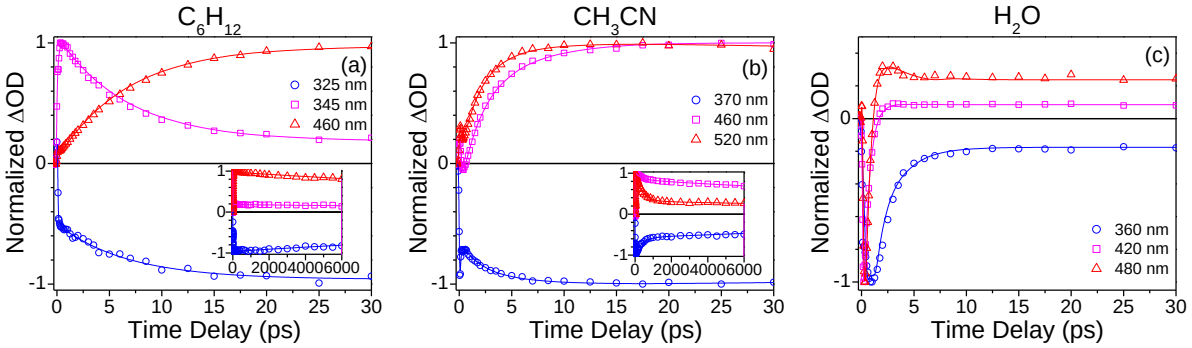

Figure S11 Experimental and fitted (—) decay profile at indicated wavelengths of the fs-TA for DMABA in (a) cyclohexane, (b) acetonitrile and (c) water. The insets in (a) and (b) show the kinetic profile at late time delay up to ~6000 ps.

Details of computational results obtained from DFT and TDDFT calculation of the ground state and the excited state of DMABA in the different solvents:

DMABA at the ground state in acetonitrile (CH_3CN)

Symbolic Z-matrix of the optimized structure:

C	1.02908	1.38273	-0.00105
C	1.85562	0.23249	-0.0004
C	1.22045	-1.04251	0.00014
C	-0.16748	-1.14841	0.00004
C	-0.98326	0.00425	-0.00068
C	-0.34696	1.2845	-0.00127
H	1.48857	2.36565	-0.00144
H	1.83379	-1.93386	0.00071
H	-0.61449	-2.13284	0.00063
H	-0.93814	2.18924	-0.00191
N	-2.37493	-0.08725	-0.00103
C	-3.01708	-1.38602	-0.00013
H	-2.72959	-1.96487	0.88718
H	-4.09527	-1.25693	-0.00191
H	-2.72691	-1.96724	-0.8849
C	-3.20275	1.10615	0.00179
H	-3.00888	1.72423	-0.88285
H	-4.24886	0.81421	-0.00081
H	-3.0115	1.71826	0.8913
C	3.31649	0.3599	-0.00022
O	4.09206	-0.63635	0.00153
H	3.71466	1.38738	-0.00026

Total energies of the optimized structure (E_{Tot}) = -479.507272 Hartree

Vibrational frequency (cm^{-1}) of the optimized structure:

(1)	52.9627	(21)	844.7987	(41)	1480.0281
(2)	69.5725	(22)	953.234	(42)	1481.5952
(3)	81.5055	(23)	963.6101	(43)	1485.7634
(4)	159.2861	(24)	987.9485	(44)	1505.4942
(5)	166.9402	(25)	1009.9148	(45)	1522.4467
(6)	181.5957	(26)	1027.3893	(46)	1559.5082
(7)	242.5855	(27)	1075.2141	(47)	1568.9061
(8)	268.8648	(28)	1130.1357	(48)	1620.0672
(9)	330.6582	(29)	1137.7117	(49)	1689.2864
(10)	341.6642	(30)	1146.6248	(50)	2908.2678
(11)	439.3437	(31)	1182.1962	(51)	3006.7588
(12)	472.6642	(32)	1194.5802	(52)	3013.6394
(13)	496.0032	(33)	1257.1531	(53)	3055.3401
(14)	516.2185	(34)	1264.5613	(54)	3057.1616
(15)	605.7915	(35)	1337.4268	(55)	3140.6923
(16)	645.5464	(36)	1367.7444	(56)	3151.6451
(17)	731.9561	(37)	1391.8713	(57)	3160.3918
(18)	734.1304	(38)	1425.8972	(58)	3180.6962
(19)	812.0984	(39)	1446.4412	(59)	3215.4911
(20)	830.9518	(40)	1468.7815	(60)	3216.6551

DMABA at the lowest energy singlet excite state in acetonitrile (CH_3CN)

Symbolic Z-matrix of the optimized structure:

C	1.02872	1.38298	-0.12051
C	1.85569	0.2327	-0.02014
C	1.22015	-1.04241	0.08023
C	-0.16736	-1.14834	0.08006
C	-0.98386	0.00431	-0.02043
C	-0.34707	1.28472	-0.13072
H	1.48815	2.36593	-0.2007
H	1.83323	-1.93391	0.15066
H	-0.61445	-2.13277	0.19038
H	-0.93837	2.18937	-0.24115
N	-2.37429	-0.08729	-0.05078
C	-3.01668	-1.38648	-0.17003
H	-2.92898	-1.96516	0.78722
H	-4.09478	-1.25732	-0.40171
H	-2.52646	-1.96728	-0.98496
C	-3.20286	1.10611	0.26132

H	-3.13912	1.87333	-0.55388
H	-4.24878	0.81378	0.34923
H	-2.8813	1.56874	1.2203
C	3.31598	0.36021	-0.01995
O	4.09248	-0.63669	0.07023
H	3.71483	1.38708	-0.11076

Total energies of the optimized structure (E_{Tot}) = -479.402023 Hartree

Vibrational frequency (cm^{-1}) of the optimized structure:

(1)	20.9627	(21)	827.4789	(41)	1437.881
(2)	67.6026	(22)	862.4195	(42)	1446.7954
(3)	87.8849	(23)	919.9794	(43)	1454.8741
(4)	144.3812	(24)	944.6791	(44)	1468.8853
(5)	150.1189	(25)	960.0146	(45)	1482.277
(6)	195.6063	(26)	988.8466	(46)	1489.1986
(7)	230.5914	(27)	1018.4457	(47)	1503.7571
(8)	259.0504	(28)	1071.6827	(48)	1551.4138
(9)	305.1378	(29)	1106.7982	(49)	1628.0145
(10)	389.6475	(30)	1128.0042	(50)	2916.1223
(11)	451.8964	(31)	1147.8255	(51)	3035.9942
(12)	469.2711	(32)	1181.8141	(52)	3037.0283
(13)	474.432	(33)	1213.5641	(53)	3098.7235
(14)	497.0867	(34)	1251.09	(54)	3104.1621
(15)	594.0465	(35)	1292.5799	(55)	3153.28
(16)	641.5855	(36)	1308.451	(56)	3165.1974
(17)	677.039	(37)	1331.2292	(57)	3169.637
(18)	709.2557	(38)	1371.1039	(58)	3178.7631
(19)	773.7675	(39)	1405.6997	(59)	3180.6762
(20)	813.1979	(40)	1415.5097	(60)	3190.659

DMABA at the ground state in cyclohexane (C_6H_{12})

Symbolic Z-matrix of the optimized structure:

C	1.03769	1.35732	0.00008
C	1.84341	0.20481	0.00007
C	1.20116	-1.04891	-0.00015
C	-0.17299	-1.15036	-0.00047
C	-0.99474	0.01505	-0.00079
C	-0.34147	1.27804	-0.00022
H	1.50999	2.33518	0.00047
H	1.80626	-1.94849	0.00005
H	-0.62548	-2.1318	-0.00042
H	-0.92003	2.1907	0.00005
N	-2.35491	-0.08057	-0.00163
C	-3.00777	-1.38695	0.00103
H	-2.74356	-1.96698	0.89139
H	-4.08544	-1.24289	-0.00142
H	-2.74042	-1.97167	-0.88521
C	-3.1798	1.12415	0.00091
H	-2.9928	1.73976	-0.88502
H	-4.22804	0.83556	-0.00234
H	-2.99644	1.73412	0.89161
C	3.29139	0.33274	0.00048
O	4.0974	-0.59287	-0.0004
H	3.65994	1.37805	-0.00022

Total energies of the optimized structure (E_{Tot}) =-479.501003 Hartree

Vibrational frequency (cm^{-1}) of the optimized structure:

(1)	26.66	(21)	846.5095	(41)	1482.2123
(2)	69.0358	(22)	956.9246	(42)	1485.1823
(3)	80.4051	(23)	958.3068	(43)	1489.4762
(4)	158.3884	(24)	987.2473	(44)	1511.0571
(5)	165.3721	(25)	1013.6765	(45)	1525.9872
(6)	186.1474	(26)	1025.8109	(46)	1558.6514
(7)	237.6328	(27)	1076.7446	(47)	1579.2668
(8)	268.4081	(28)	1134.026	(48)	1635.3147
(9)	331.998	(29)	1136.4199	(49)	1720.5545
(10)	341.3259	(30)	1147.6133	(50)	2887.813
(11)	437.7698	(31)	1186.5613	(51)	2999.3957
(12)	471.7243	(32)	1194.3988	(52)	3006.5559
(13)	494.8978	(33)	1258.5636	(53)	3044.765

(14)	517.6183	(34)	1263.2168	(54)	3047.3774
(15)	606.875	(35)	1337.5982	(55)	3131.3898
(16)	647.2256	(36)	1366.8842	(56)	3143.9066
(17)	731.7614	(37)	1389.9599	(57)	3156.6813
(18)	736.0826	(38)	1423.1089	(58)	3182.5099
(19)	812.7254	(39)	1447.0381	(59)	3212.1274
(20)	831.1014	(40)	1468.4102	(60)	3213.1765

DMABA at the lowest energy singlet excite state in cyclohexane (C_6H_{12})

Symbolic Z-matrix of the optimized structure:

C	1.02614	1.38553	-0.01023
C	1.86784	0.22835	-0.00993
C	1.2113	-1.04425	-0.01031
C	-0.16484	-1.13932	0.0189
C	-0.99449	0.0112	0.06821
C	-0.34345	1.2786	0.01896
H	1.47974	2.3709	-0.03967
H	1.80523	-1.9503	-0.03983
H	-0.60873	-2.1258	0.00879
H	-0.9291	2.18789	0.00893
N	-2.37117	-0.08862	0.21649
C	-3.00935	-1.39458	-0.09857
H	-2.57113	-2.23634	0.56204
H	-4.08977	-1.26398	0.15853
H	-2.90766	-1.72381	-1.223
C	-3.19424	1.10963	-0.10838
H	-3.14312	1.44276	-1.23271
H	-4.24363	0.82123	0.14844
H	-2.88579	2.01438	0.54254
C	3.25514	0.35202	-0.00908
O	4.1285	-0.62213	-0.00853
H	3.73997	1.33733	-0.01868

Total energies of the optimized structure (E_{Tot}) = -479.372559 Hartree

Vibrational frequency (cm^{-1}) of the optimized structure:

(1)	62.8444	(21)	795.8349	(41)	1465.7361
(2)	71.5393	(22)	821.8394	(42)	1483.3131
(3)	126.1834	(23)	926.1305	(43)	1484.1051
(4)	146.4878	(24)	946.373	(44)	1489.927
(5)	176.5315	(25)	949.5798	(45)	1504.463
(6)	188.7326	(26)	991.6302	(46)	1518.8421
(7)	249.9625	(27)	1075.7743	(47)	1529.1468
(8)	276.3408	(28)	1121.8422	(48)	1534.1018
(9)	340.4768	(29)	1123.7313	(49)	1623.3962
(10)	360.8924	(30)	1140.3036	(50)	2965.1545
(11)	422.0539	(31)	1146.2474	(51)	2971.766
(12)	452.6547	(32)	1182.4597	(52)	3006.2135
(13)	480.7805	(33)	1193.746	(53)	3061.3735
(14)	493.0505	(34)	1231.1709	(54)	3062.2245
(15)	552.4849	(35)	1244.9005	(55)	3118.6906
(16)	588.0685	(36)	1332.9116	(56)	3128.7748
(17)	642.7342	(37)	1345.974	(57)	3165.9234
(18)	696.7756	(38)	1374.4357	(58)	3180.6459
(19)	705.7467	(39)	1411.6133	(59)	3205.7121
(20)	780.0318	(40)	1443.6992	(60)	3207.5931

DMABA at the ground state in water (H_2O)

Symbolic Z-matrix of the optimized structure:

C	-7.95648	-0.03672	-4.47972
C	-6.78442	-0.85765	-4.45454
C	-6.96845	-2.27008	-4.56453
C	-8.2375	-2.81322	-4.66718
C	-9.38492	-2.00017	-4.67687
C	-9.20461	-0.59626	-4.59121
H	-7.85362	1.04127	-4.42644
H	-6.1058	-2.92546	-4.55563
H	-8.33253	-3.8892	-4.73316
H	-10.07146	0.04953	-4.65895
N	-10.70297	-2.51411	-4.81534
C	-10.82534	-3.92565	-5.17913

H	-10.51845	-4.60416	-4.3697
H	-11.87015	-4.13194	-5.41622
H	-10.22463	-4.13849	-6.06396
C	-11.63297	-2.15515	-3.72971
H	-11.57783	-1.08984	-3.51477
H	-12.65251	-2.39064	-4.04013
H	-11.40882	-2.70995	-2.80765
C	-5.51476	-0.28296	-4.34179
O	-4.37664	-0.90986	-4.32343
H	-5.38878	0.80631	-4.26547
O	-11.89689	-0.78374	-6.8497
H	-11.48343	-1.42875	-6.2429
H	-12.69477	-0.51172	-6.38489
O	-1.73732	-1.07134	-4.69945
H	-1.36055	-0.99715	-3.81717
H	-2.72366	-1.0327	-4.56815

Total energies of the optimized structure (E_{Tot}) = -632.402474 Hartree

Vibrational frequency (cm^{-1}) of the optimized structure:

(1)	22.7783	(27)	646.7407	(53)	1477.9689
(2)	28.9387	(28)	656.2348	(54)	1488.906
(3)	32.3768	(29)	735.8352	(55)	1495.2735
(4)	36.0961	(30)	738.3302	(56)	1501.9008
(5)	43.3602	(31)	820.8772	(57)	1521.485
(6)	73.1517	(32)	841.1843	(58)	1548.7069
(7)	81.1714	(33)	853.0678	(59)	1577.0281
(8)	90.8174	(34)	944.0272	(60)	1618.4451
(9)	110.1811	(35)	971.6443	(61)	1622.0381
(10)	126.9127	(36)	992.8288	(62)	1628.2681
(11)	163.537	(37)	1014.1413	(63)	1682.0916
(12)	169.067	(38)	1033.9601	(64)	2948.4222
(13)	181.3252	(39)	1065.1053	(65)	3006.6898
(14)	217.1784	(40)	1119.4137	(66)	3011.3145
(15)	249.1034	(41)	1142.3635	(67)	3098.6062
(16)	306.3384	(42)	1149.3994	(68)	3101.3333
(17)	318.574	(43)	1186.5023	(69)	3136.2442
(18)	336.6125	(44)	1196.711	(70)	3144.6044
(19)	366.0644	(45)	1234.0745	(71)	3167.4375
(20)	372.6943	(46)	1267.9474	(72)	3187.0638
(21)	433.4434	(47)	1341.3326	(73)	3224.1216
(22)	468.21	(48)	1356.4088	(74)	3225.5305
(23)	493.7323	(49)	1364.6758	(75)	3529.8618
(24)	524.3388	(50)	1427.0548	(76)	3652.9715
(25)	529.4068	(51)	1447.1346	(77)	3860.7979
(26)	605.3409	(52)	1464.3031	(78)	3862.5011

DMABA at the lowest energy singlet excite state in in water (H_2O)

Symbolic Z-matrix of the optimized structure:

C	1.24936	1.27596	0.43134
C	2.18825	0.25959	0.06563
C	1.66515	-1.02062	-0.29263
C	0.30277	-1.26337	-0.26065
C	-0.61209	-0.26305	0.11365
C	-0.09798	1.01564	0.44752
H	1.60811	2.26778	0.68246
H	2.34286	-1.81501	-0.58146
H	-0.04977	-2.25177	-0.52504
H	-0.79026	1.81587	0.67869
N	-2.01981	-0.45982	0.12649
C	-2.51911	-1.69027	-0.48706
H	-2.26879	-2.59006	0.09386
H	-3.60585	-1.62447	-0.55822
H	-2.11557	-1.79776	-1.49438
C	-2.67767	-0.19709	1.41899
H	-2.34503	0.75317	1.83186
H	-3.75725	-0.14638	1.26665
H	-2.46215	-0.99011	2.149
C	3.56002	0.52978	0.04965
O	4.51073	-0.29384	-0.27665

H	3.94691	1.52226	0.32081
O	-3.04962	1.90833	-1.24815
H	-2.71745	1.0682	-0.87526
H	-3.68808	2.21171	-0.59471
O	7.09701	-0.2192	-0.49018
H	7.3912	-0.25823	0.42516
H	6.15553	-0.5433	-0.47867

Total energies of the optimized structure (E_{Tot}) =-632.240551 Hartree

Vibrational frequency (cm^{-1}) of the optimized structure:

(1)	32.5771	(27)	642.3354	(53)	1464.3403
(2)	41.8528	(28)	699.2838	(54)	1472.5204
(3)	55.362	(29)	700.8825	(55)	1480.8051
(4)	72.9272	(30)	709.7636	(56)	1492.5312
(5)	82.5538	(31)	727.5831	(57)	1498.2321
(6)	95.5796	(32)	793.7168	(58)	1512.2048
(7)	104.7928	(33)	812.2444	(59)	1529.4515
(8)	119.3227	(34)	838.0527	(60)	1535.2336
(9)	157.1924	(35)	937.9043	(61)	1615.919
(10)	164.9052	(36)	942.2226	(62)	1627.1926
(11)	187.5421	(37)	959.1344	(63)	1677.7618
(12)	203.7642	(38)	1000.8526	(64)	2969.4336
(13)	228.7967	(39)	1056.9703	(65)	2975.758
(14)	277.5981	(40)	1112.3989	(66)	3075.3996
(15)	278.2713	(41)	1132.7629	(67)	3079.1247
(16)	296.7515	(42)	1149.3856	(68)	3117.4566
(17)	306.5928	(43)	1171.3747	(69)	3121.5946
(18)	328.2795	(44)	1178.103	(70)	3133.9291
(19)	390.066	(45)	1199.1399	(71)	3164.2338
(20)	406.9612	(46)	1202.6263	(72)	3178.417
(21)	425.5252	(47)	1229.2501	(73)	3185.4867
(22)	436.9236	(48)	1317.444	(74)	3197.1338
(23)	439.4822	(49)	1331.7603	(75)	3493.8813
(24)	489.6095	(50)	1340.0008	(76)	3791.1384
(25)	525.428	(51)	1416.3155	(77)	3854.693
(26)	570.6854	(52)	1442.8663	(78)	3876.6827

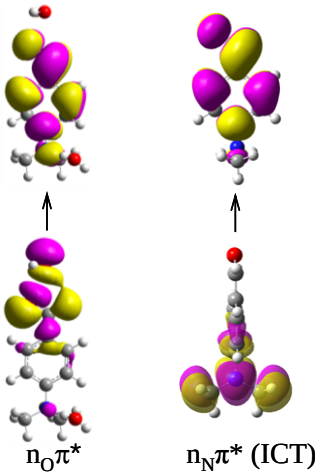

Figure S12 Diagram of the molecular orbital calculated for the DMABA (left) $n_O\pi^*$ state in H_2O and (right) $n_N\pi^*$ (ICT) state in CH_3CN.