Supplymentary Materials

Nonlinear Optical Study in a Set of Dibenzylideneacetone Derivatives with Potential for Optical Frequency Conversion

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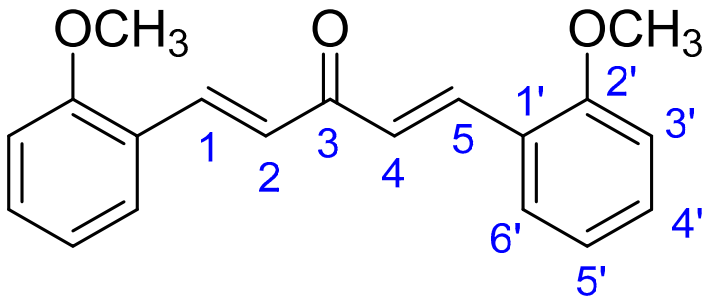
Received: 30 November 2019; Accepted: 6 January 2020; Published: date

1. Results of RMN characterization



(1*E*,4*E*)-1,5-bis(2′-methoxyphenyl)penta-1,4-dien-3-one (2-DMDBA): ^{1}H NMR, 500 MHz, $CDCl_3$, ✾ **3.8**9 (6H, s, 2 x OCH_3), 6.91 (2H, d, *J* = 8.2 Hz, H3′), 6.97 (2H, t, *J* = 7.5 Hz, H5′), 7.16 (2H, d, *J* = 16.3 Hz, H2, H4), 7.35 (2H, dt, *J* = 8.2 Hz, *J* = 1.6 Hz, H4′), 7.60 (2H, dd, *J* = 1.6 Hz, *J* = 7.5 Hz, H6′), 8.05 (2H, d, *J* = 16.3 Hz, H1, H5). NMR ^{13}C, 125 MHz, $CDCl_3$, ⌾ 5.7 (OCH_3), 111.4 (C3′), 120.9 (C5′), 124.2 (C1′), 126.5 (C2, C4), 128.9, 131.7 (C4′, C6′), 138.4 (C1, C5), 158.8 (C2′), 190.2 (C3).

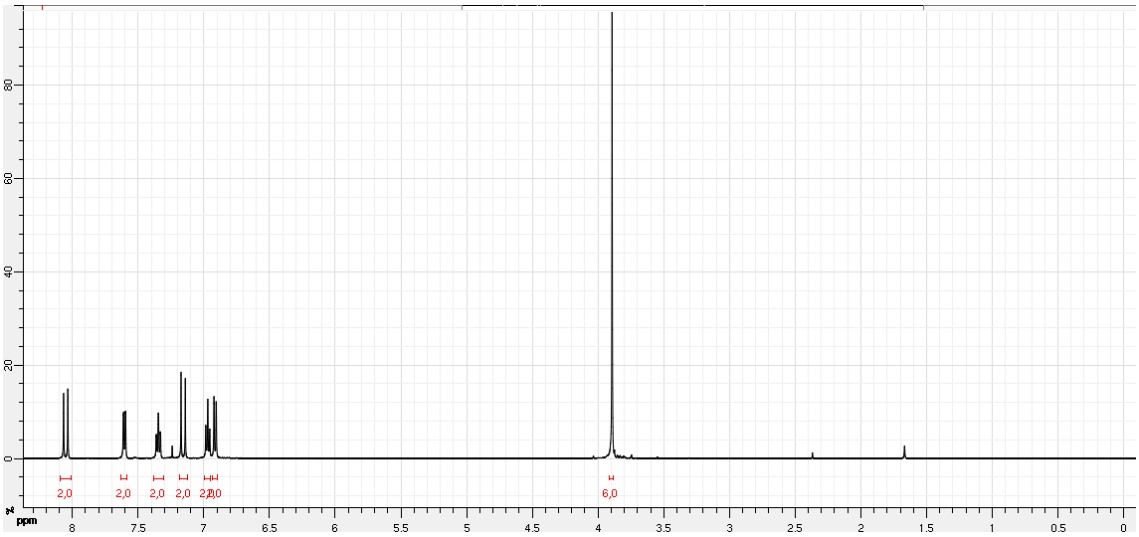


Figure S1. [1]H NMR Spectra of compound **2-DMDBA**.

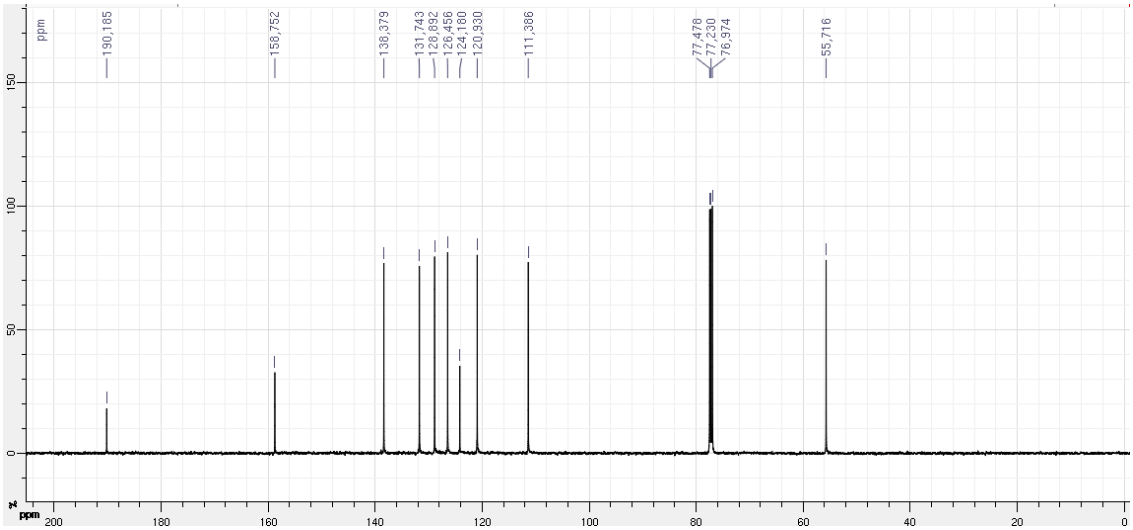
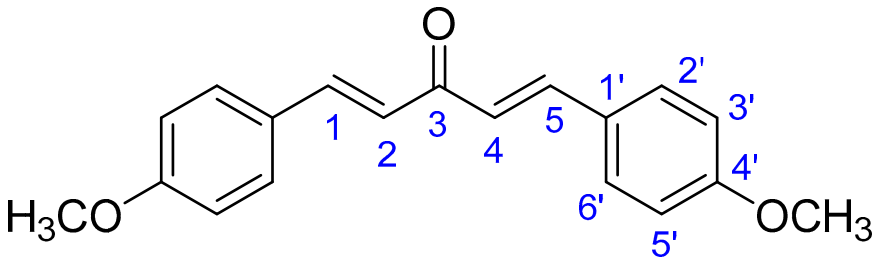


Figure S2. [13]C NMR Spectra of compound 2-DMDBA.



(1*E*,4*E*)-1,5-bis(4-methoxyphenyl)penta-1,4-dien-3-one (4-DMDBA): [1]H NMR, 500 MHz, $CDCl_3$, ✾ **3.82** (6H, s, 2 x OCH_3), 6.90 (4H, d, *J* = 8.8 Hz, H3′, H5′), 6.93 (2H, d, *J* = 15.7 Hz, H2, H4), 7.54 (4H, d, *J* = 8.8 Hz, H2′, H6′), 7.67 (2H, d, *J* = 15.7 Hz, H1, H5). NMR [13]C, 125 MHz, $CDCl_3$, ⌾ 55.4 (OCH_3), 114.4 (C3′), 123.5 (C2′, C6′), 127.7 (C1), 130.1 (C2, C4), 142.7 (C1, C5), 161.6 (C4′), 188.9 (C3).

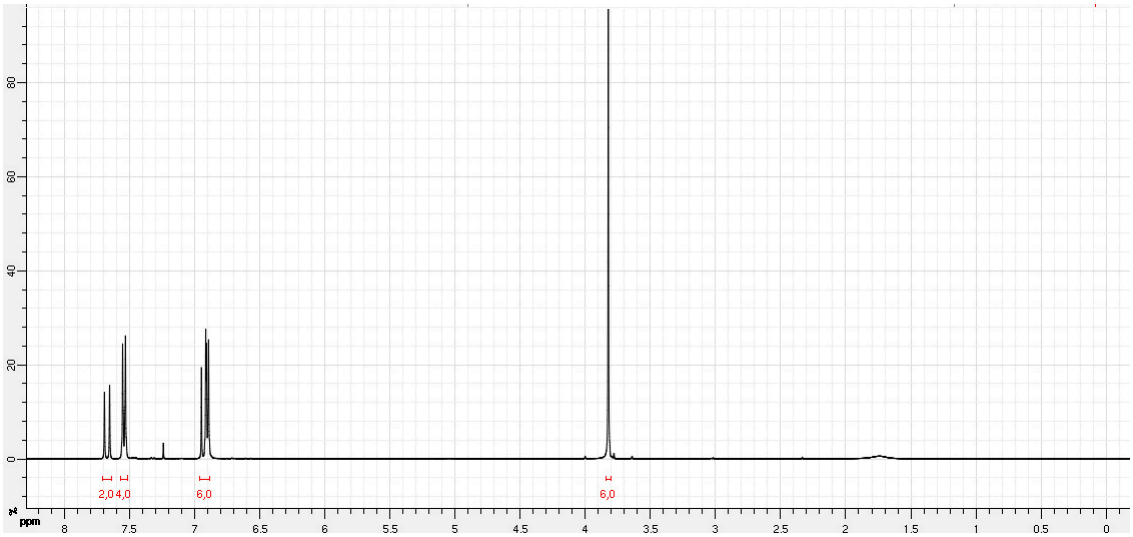


Figure S3. [1]H NMR spectra of compound 4-DMDBA.

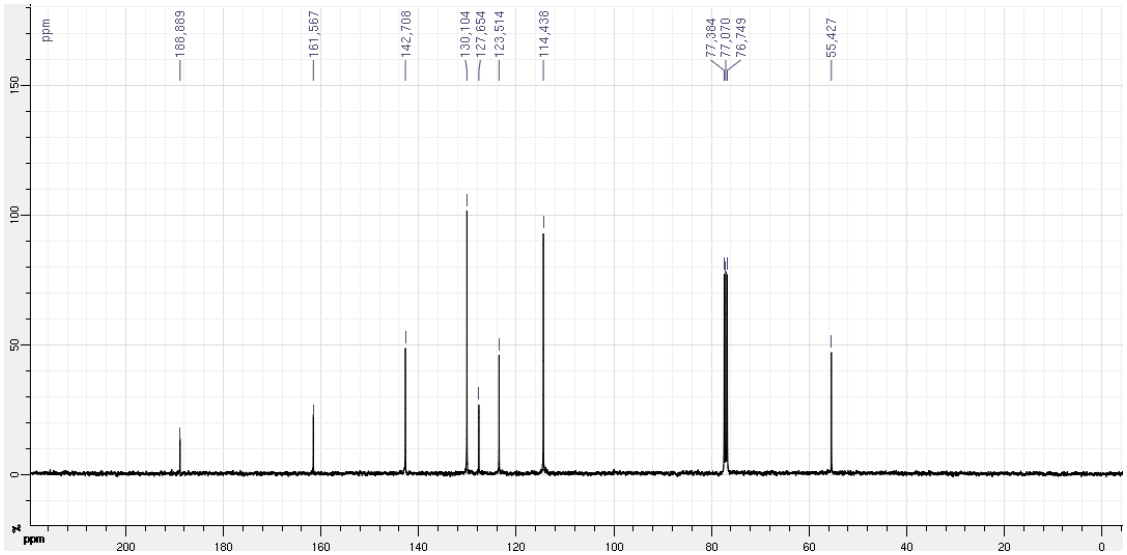
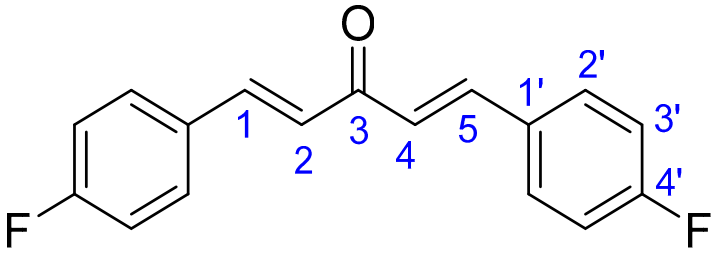


Figure S4. [13]C NMR spectra of compound **4-DMDBA**.



(1*E*,4*E*)-1,5-bis(4′-fluorophenyl)penta-1,4-dien-3-one (4-DFDBA). NMR [1]H, 500 MHz, $CDCl_3$, ◎ 6.96 (2H, d, *J* = 15.7 Hz, H2), 7.08 (4H, t, *J* = 8.5 Hz, H2′), 7.58 (4H, td, *J* = 8.5 Hz, *J* = 2.2 Hz, H3′), 7.67 (2H, d, *J* = 15.7 Hz, H1). NMR [13]C, 125 MHz, $CDCl_3$, ◎ 116.3 (d, *J* = 21,1 Hz, C3′), 125.3 (C2), 130.5 (d, *J* = 8.0 Hz, C2′), 131.2 (d, *J* = 3.0 Hz, C1′), 142.3 (s, C1), 164.2 (d, *J* = 252.0 Hz, C4′), 188.6 (C=O).

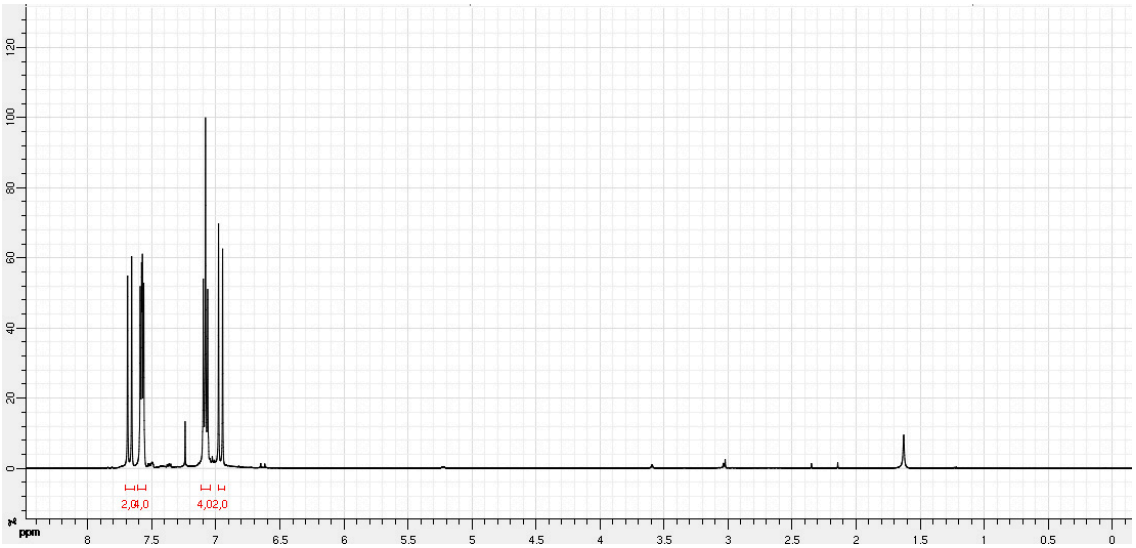


Figure S5. [1]H NMR spectra of compound 4-DFDBA.

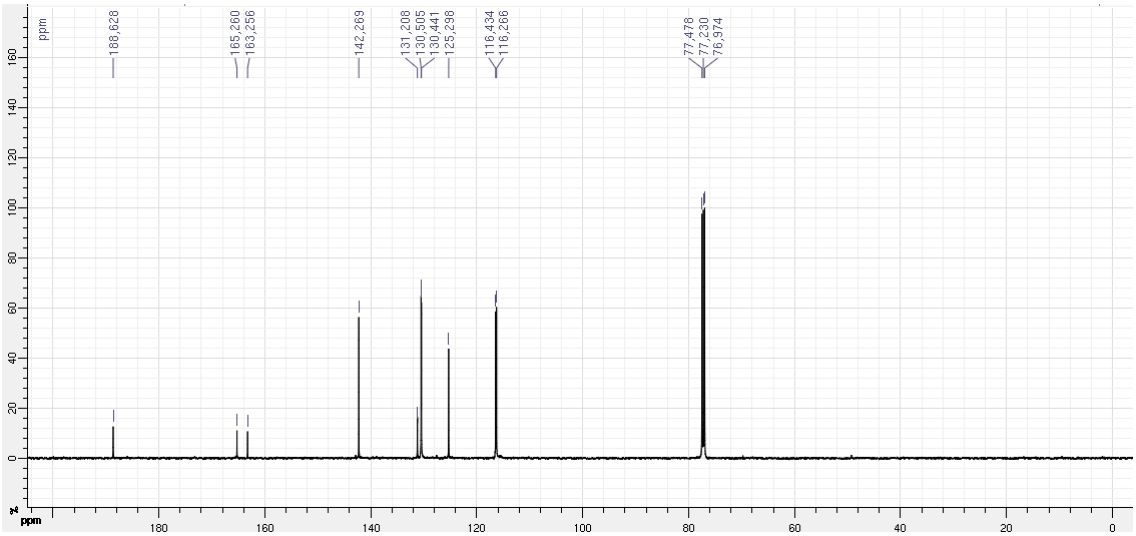


Figure S6. [13]C NMR spectra of compound 4-DFDBA.

2. Optimized geometries

Table S1. Optimized geometries for 4-DMDBA and 2-DMDBA.

Sample: 4-DBDBA				**Sample: 2-DMDBA**			
Solvent (PCM, solvent=Dichloromethane)				Solvent (PCM, solvent=Dichloromethane)			
O	0.00000	2.39749	-0.00002	O	-0.00011	1.60353	0.33867
C	0.00000	1.17118	-0.00006	C	0.00001	0.39203	0.15922
C	1.24850	0.38736	-0.00010	C	1.24960	-0.38503	0.04365
H	1.15252	-0.69129	-0.00020	H	1.14963	-1.45105	-0.11867
C	2.44222	0.98808	-0.00000	C	2.44246	0.21010	0.12689
H	2.43533	2.07428	0.00011	H	2.44116	1.28405	0.26690
C	3.75746	0.36512	-0.00001	C	3.75148	-0.42708	0.04285
C	3.95320	-1.02291	-0.00015	C	3.91439	-1.81123	0.05613
H	3.10223	-1.69153	-0.00027	H	3.03967	-2.44274	0.13982
C	5.21624	-1.56100	-0.00015	C	5.16283	-2.39751	-0.01945
C	6.33802	-0.72769	-0.00001	C	6.28565	-1.59020	-0.10851
O	7.53661	-1.35223	-0.00002	H	7.27166	-2.03385	-0.16706
C	6.16990	0.65043	0.00014	C	6.16415	-0.21069	-0.11994

H	7.01856	1.31791	0.00025	H	7.05176	0.39985	-0.18919
H	5.36671	-2.63277	-0.00026	H	5.26090	-3.47479	-0.00367
C	4.88767	1.17669	0.00013	C	4.90582	0.37520	-0.04428
H	4.76385	2.25314	0.00024	C	-1.24941	-0.38513	0.04257
C	-1.24850	0.38736	-0.00005	H	-1.14918	-1.45104	-0.12028
H	-1.15252	-0.69129	-0.00005	C	-2.44238	0.20981	0.12577
C	-2.44222	0.98808	-0.00003	C	-3.75137	-0.42729	0.04068
C	-3.75746	0.36512	-0.00002	C	-4.90587	0.37512	-0.04316
C	-4.88767	1.17669	0.00004	C	-6.16419	-0.21070	-0.11976
H	-4.76385	2.25314	0.00007	H	-7.05192	0.39995	-0.18648
C	-6.16990	0.65043	0.00006	C	-6.28552	-1.59024	-0.11255
H	-7.01856	1.31791	0.00010	H	-7.27152	-2.03382	-0.17180
C	-6.33802	-0.72769	0.00001	C	-5.16253	-2.39769	-0.02682
O	-7.53661	-1.35223	0.00002	H	-5.26046	-3.47503	-0.01444
C	-5.21624	-1.56100	-0.00006	C	-3.91413	-1.81151	0.04970
H	-5.36671	-2.63277	-0.00010	H	-3.03929	-2.44321	0.13057
C	-3.95320	-1.02291	-0.00007	H	-2.44119	1.28364	0.26676
H	-3.10223	-1.69153	-0.00013	O	-4.70944	1.71361	-0.05141
H	-2.43533	2.07428	-0.00002	O	4.70916	1.71363	-0.05666
C	8.71307	-0.55635	0.00015	C	-5.83898	2.57066	-0.11456
H	9.54563	-1.25378	0.00012	H	-5.44504	3.58270	-0.09671
H	8.76285	0.06985	0.89290	H	-6.49543	2.42047	0.74452
H	8.76296	0.07006	-0.89246	H	-6.39936	2.41498	-1.03822
C	-8.71307	-0.55635	0.00011	C	5.83854	2.57064	-0.12313
H	-9.54563	-1.25379	0.00012	H	5.44447	3.58269	-0.10823
H	-8.76295	0.06999	-0.89254	H	6.39840	2.41215	-1.04663
H	-8.76286	0.06992	0.89282	H	6.49550	2.42323	0.73603

Table S2. Optimized geometries for 4-DFDBA.

Sample: 4-DFDBA				**Sample: PNA (Reference Sample)**			
Solvent (PCM, solvent=Dichloromethane)				Solvent (PCM, solvent=Dichloromethane)			
O	0.00000	2.34044	0.00033	O	2.73482	1.07542	0.00355
C	0.00000	1.11684	0.00015	O	2.73482	-1.07542	0.00365
C	-1.25072	0.33187	0.00011	N	2.14738	0.00000	0.00200
H	-1.15460	-0.74660	-0.00001	N	-3.43167	0.00000	-0.03027
C	-2.44116	0.93411	0.00017	C	-1.35557	1.21195	-0.00395
H	-2.43577	2.01995	0.00019	C	0.01886	1.21159	-0.00253
C	-3.75926	0.30622	0.00014	C	0.70676	0.00000	-0.00175
C	-3.94343	-1.07916	0.00101	C	0.01886	-1.21159	-0.00257
H	-3.08926	-1.74270	0.00185	C	-1.35557	-1.21195	-0.00400
C	-5.20947	-1.62832	0.00088	C	-2.07356	0.00000	-0.00313
C	-6.29615	-0.77678	-0.00013	H	-1.89495	2.15121	-0.00573
F	-7.53439	-1.31189	-0.00025	H	0.56940	2.14155	-0.00120
C	-6.16562	0.59303	-0.00096	H	0.56940	-2.14155	-0.00127
H	-7.04509	1.22234	-0.00170	H	-1.89495	-2.15121	-0.00581
H	-5.36381	-2.69880	0.00156	H	-3.93735	0.85549	0.13092
C	-4.88833	1.12559	-0.00079	H	-3.93735	-0.85550	0.13089
H	-4.76293	2.20119	-0.00142				
C	1.25072	0.33187	-0.00000				
H	1.15460	-0.74660	-0.00019				
C	2.44116	0.93412	0.00011				
C	3.75926	0.30622	0.00000				

C	4.88833	1.12559	0.00029
H	4.76293	2.20119	0.00057
C	6.16562	0.59303	0.00022
H	7.04509	1.22234	0.00044
C	6.29615	-0.77678	-0.00015
F	7.53439	-1.31189	-0.00022
C	5.20946	-1.62832	-0.00045
H	5.36381	-2.69880	-0.00074
C	3.94344	-1.07916	-0.00037
H	2.43577	2.01995	0.00032
H	3.08926	-1.74270	-0.00061

3. Z-Scan signatures

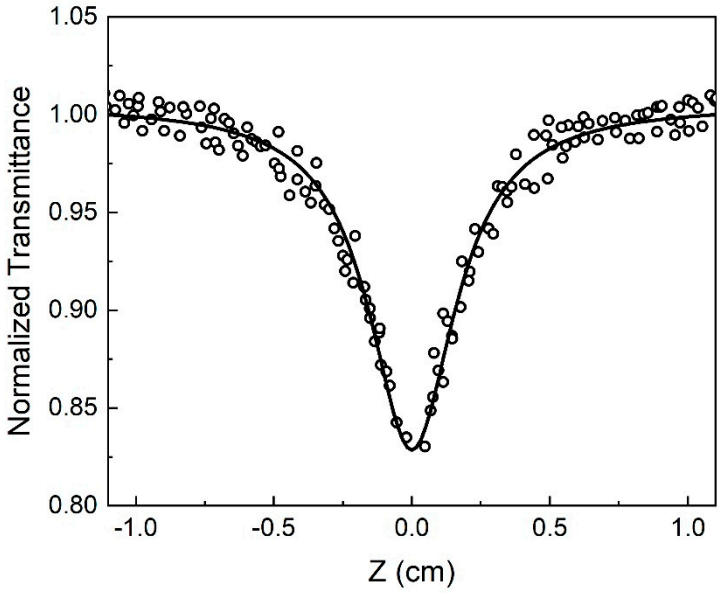


Figure S7. Open aperture Z-scan signature for 4-DFDBA in dichloromethane solution when excited with a femtosecond pulse tuned at 610 nm, where the circles represent the experimental values and the solid line is the fitting obtained with Equation 3.

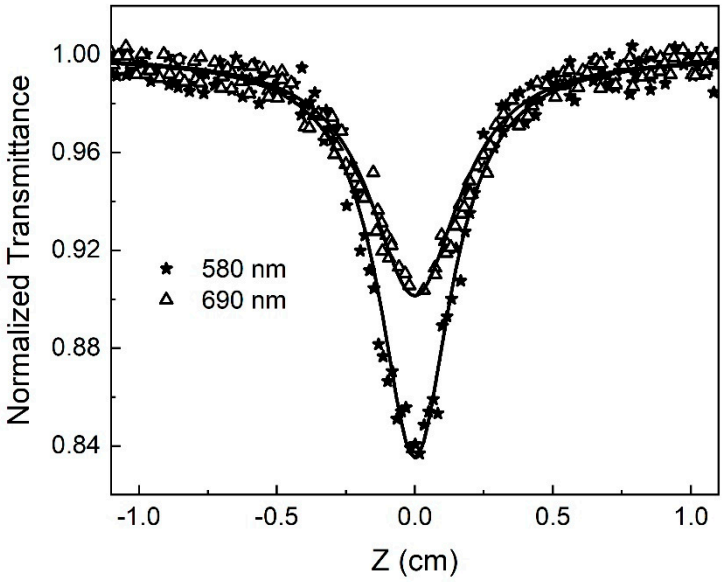


Figure S8. Open aperture Z-scan signature for 2-DMDBA in dichloromethane solution when excited with a femtosecond pulse tuned at 580 nm and 690nm, where the symbols represent the experimental values while the solid line is the fitting obtained with Equation 3.

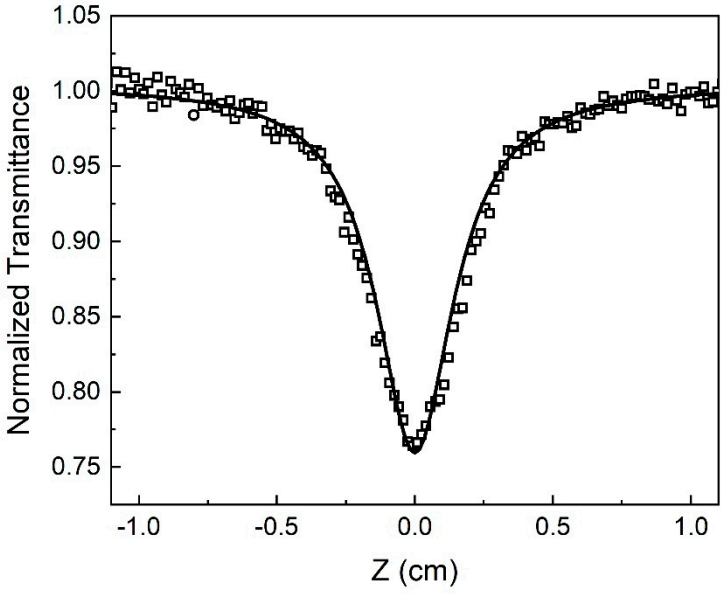


Figure S9. Open aperture Z-scan signature for 4-DMDBA in dichloromethane solution when excited with a femtosecond pulse tuned at 660 nm, where the squares represent the experimental values while the solid line is the fitting obtained with Equation 3.

4. Frequencies transitions and oscillator strength

Table S3. Excited states, transition energy, and oscillator strength for 4-DMDBA.

Sample: 4-DMDBA, DCM							
CAM-B3LYP/6-311+G(d,p)				**B3LYP/6-311+G(d,p)**			
excited state	**eV**	**nm**	**f**	**excited state**	eV	nm	f
1	3.5247	351.76	1.9539	1	2.9351	422.42	1.7770
2	3.5897	345.39	0.0000	2	3.1758	390.41	0.0000
3	4.0499	306.14	0.1342	3	3.4042	364.21	0.0949
4	4.8441	255.95	0.0065	4	4.2055	294.81	0.0019
5	4.8446	255.92	0.0065	5	4.2066	294.74	0.0006
6	5.4575	227.18	0.0614	6	4.5742	271.05	0.1424
7	5.5995	221.42	0.0323	7	4.6842	264.68	0.3044
8	5.6380	219.91	0.2790	8	4.8208	257.18	0.2544
9	5.6998	217.52	0.2552	9	4.8496	255.66	0.0391
10	5.9405	208.71	0.0000	10	4.9366	251.15	0.0007
11	5.9522	208.30	0.0152	11	4.9941	248.26	0.0403
12	5.9833	207.22	0.0274	12	5.0219	246.89	0.0001
13	6.0530	204.83	0.1932	13	5.1185	242.23	0.0066
14	6.2353	198.84	0.0002	14	5.1332	241.53	0.0419
15	6.3638	194.83	0.0000	15	5.4669	226.79	0.0000
Sample: 4-DMDBA, DCM.							
M062X/6-311+G(d,p)							
excited state	eV	nm	f				
1	3.5387	350.36	1.9404				
2	3.5441	349.84	0.0000				
3	4.0275	307.84	0.1258				
4	4.8753	254.31	0.0072				
5	4.8763	254.26	0.0063				
6	5.4321	228.24	0.0826				
7	5.5784	222.26	0.0127				
8	5.6362	219.98	0.2324				
9	5.6996	217.53	0.3680				
10	5.8164	213.16	0.0000				
11	5.8721	211.14	0.0235				
12	5.9603	208.02	0.0103				
13	6.0591	204.62	0.1737				
14	6.1792	200.65	0.0000				
15	6.2806	197.41	0.0000				

Table S4. Excited states, transition energy, and oscillator strength for 2-DMDBA.

Sample: 2-DMDBA, DCM							
CAM-B3LYP/6-311+G(d,p)				**B3LYP/6-311+G(d,p)**			
excited state	**eV**	**nm**	**f**	**excited state**	eV	nm	f
1	3.4746	356.83	1.3807	1	2.8905	428.93	1.3152
2	3.5288	351.35	0.2004	2	3.0920	400.98	0.0000
3	3.9178	316.47	0.0136	3	3.2370	383.02	0.0024
4	4.4997	275.54	0.0706	4	3.6751	337.36	0.2091
5	4.5844	270.45	0.1642	5	3.7990	326.36	0.1061

6	5.3243	232.86	0.0521	6	4.3739	283.46	0.0217
7	5.4645	226.89	0.0787	7	4.4522	278.48	0.2402
8	5.7542	215.47	0.1667	8	4.8137	257.56	0.0001
9	5.8226	212.94	0.0133	9	4.9871	248.61	0.1179
10	6.0369	205.38	0.0000	10	5.0111	247.42	0.0367
11	6.0470	205.03	0.0007	11	5.2644	235.52	0.0203
12	6.0745	204.11	0.0009	12	5.2966	234.08	0.0139
13	6.2902	197.11	0.1632	13	5.4872	225.95	0.0475
14	6.3581	195.00	0.0857	14	5.5012	225.38	0.3330
15	6.3649	194.79	0.8528	15	5.5756	222.37	0.0000

Sample: 2-DMDBA, DCM			
	M062X/6-311+G(d,p)		
excited state	eV	nm	f
1	3.4439	360.01	0.3762
2	3.5807	346.26	1.1680
3	3.9438	314.38	0.0204
4	4.5446	272.82	0.0791
5	4.6150	268.66	0.1494
6	5.3271	232.74	0.0554
7	5.4531	227.37	0.1078
8	5.7797	214.52	0.1066
9	5.8554	211.74	0.0316
10	5.9251	209.25	0.0011
11	5.9699	207.68	0.0012
12	6.2206	199.31	0.0022
13	6.2417	198.64	0.0750
14	6.2598	198.06	0.0068
15	6.3241	196.05	0.0246

Table S5. Excited states, transition energy, and oscillator strength for 4-DFDBA.

Sample: 4-DFDBA, DCM							
CAM-B3LYP/6-311+G(d,p)				**B3LYP/6-311+G(d,p)**			
excited state	**eV**	**nm**	**f**	**excited state**	eV	nm	f
1	3.5388	350.35	0.0000	1	3.1246	396.80	0.0000
2	3.7929	326.88	1.7155	2	3.2232	384.66	1.5370
3	4.2944	288.71	0.1330	3	3.6737	337.49	0.0941
4	4.9541	250.26	0.0028	4	4.2336	292.86	0.0112
5	4.9549	250.23	0.0000	5	4.2337	292.85	0.0078
6	5.6484	219.50	0.1222	6	4.8076	257.89	0.1402
7	5.7635	215.12	0.0387	7	4.8882	253.64	0.2483
8	5.9291	209.11	0.1929	8	4.9368	251.15	0.0001
9	5.9737	207.55	0.3146	9	5.0385	246.07	0.2301
10	6.1562	201.40	0.0001	10	5.1061	242.82	0.0027
11	6.2603	198.05	0.0002	11	5.2552	235.93	0.0000
12	6.3921	193.97	0.2477	12	5.3643	231.13	0.0696
13	6.4316	192.77	0.0000	13	5.3680	230.97	0.0004
14	6.5116	190.40	0.0091	14	5.3992	229.63	0.0003
15	6.6793	185.62	0.4753	15	5.6863	218.04	0.0000

Sample: 4-DFDBA, DCM			
M062X/6-311+G(d,p)			
excited state	eV	nm	f
1	3.4934	354.91	0.0000
2	3.8129	325.17	1.7050
3	4.2759	289.96	0.1246
4	4.9794	248.99	0.0017
5	4.9812	248.90	0.0000
6	5.6297	220.23	0.1450
7	5.7465	215.76	0.0275
8	5.9149	209.61	0.1402
9	5.9604	208.01	0.3983
10	6.2712	197.70	0.0001
11	6.2803	197.42	0.0000
12	6.3109	196.46	0.0000
13	6.3744	194.50	0.0085
14	6.4126	193.35	0.1857
15	6.6299	187.01	0.0000

Table S6. Spectroscopic parameters obtained through the SOS fitting of the experimental TPA spectra.

SOS parameters	**4-DMDBA**	**2-DMDBA**	**4-DFDBA**
$\boldsymbol{\mu_{0k}}$ (D)	7.30	6.88	6.85
$\boldsymbol{\mu_{kf}}$ (D)	8.58	6.73	6.10
$\boldsymbol{\mu_{kf'}}$(D)	9.41	7.80	2.03
$\boldsymbol{\mu_{kf''}}$(D)	-	4.51	-
$\boldsymbol{\omega_{0k}}$ (×10^{15} rad Hz)	5.40	5.32	5.29
$\boldsymbol{\omega_{kf}}$ (×10^{15} rad Hz)	5.67	5.34	6.12
$\boldsymbol{\omega_{kf'}}$ (×10^{15} rad Hz)	7.54	6.28	8.04
$\boldsymbol{\omega_{kf''}}$ (×10^{15} rad Hz)	-	6.86	-
$\boldsymbol{\Gamma_{0k}}$ (×10^{14} rad Hz)	3.87	3.92	4.10
$\boldsymbol{\Gamma_{0f}}$ (×10^{14} rad Hz)	3.59	3.24	5.40
$\boldsymbol{\Gamma_{0f'}}$ (×10^{14} rad Hz)	4.73	4.11	3.64
$\boldsymbol{\Gamma_{0f''}}$ (×10^{14} rad Hz)	-	4.41	-