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

SUPPORTING INFORMATION

Interplay of Twist Angle and Solvents With Two-Photon Optical Channel Interference in Aryl-Substituted BODIPY Dyes

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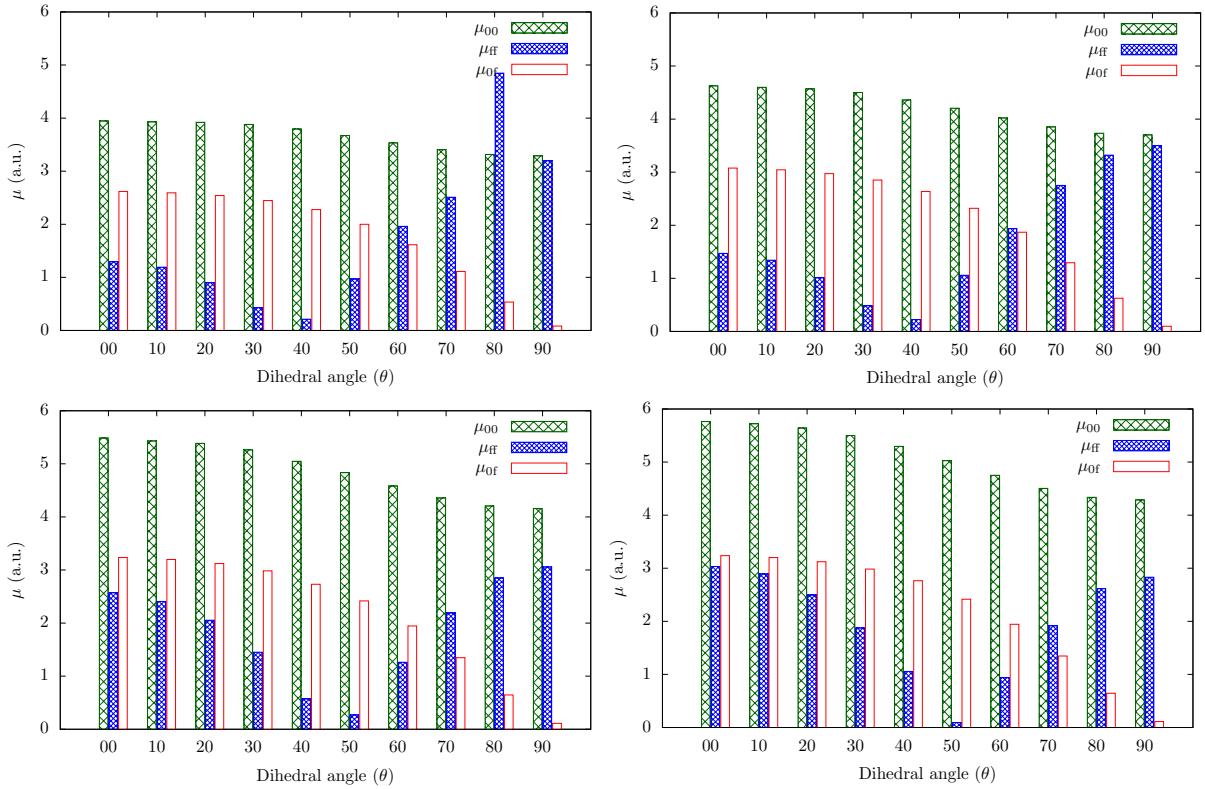

Figure S1: Variation of different μ terms involved in 2SM in vacuum (top left panel), in C_6H_{12} (top right panel), in CH_2Cl_2 (bottom left panel) and in CH_3CN (bottom right panel).

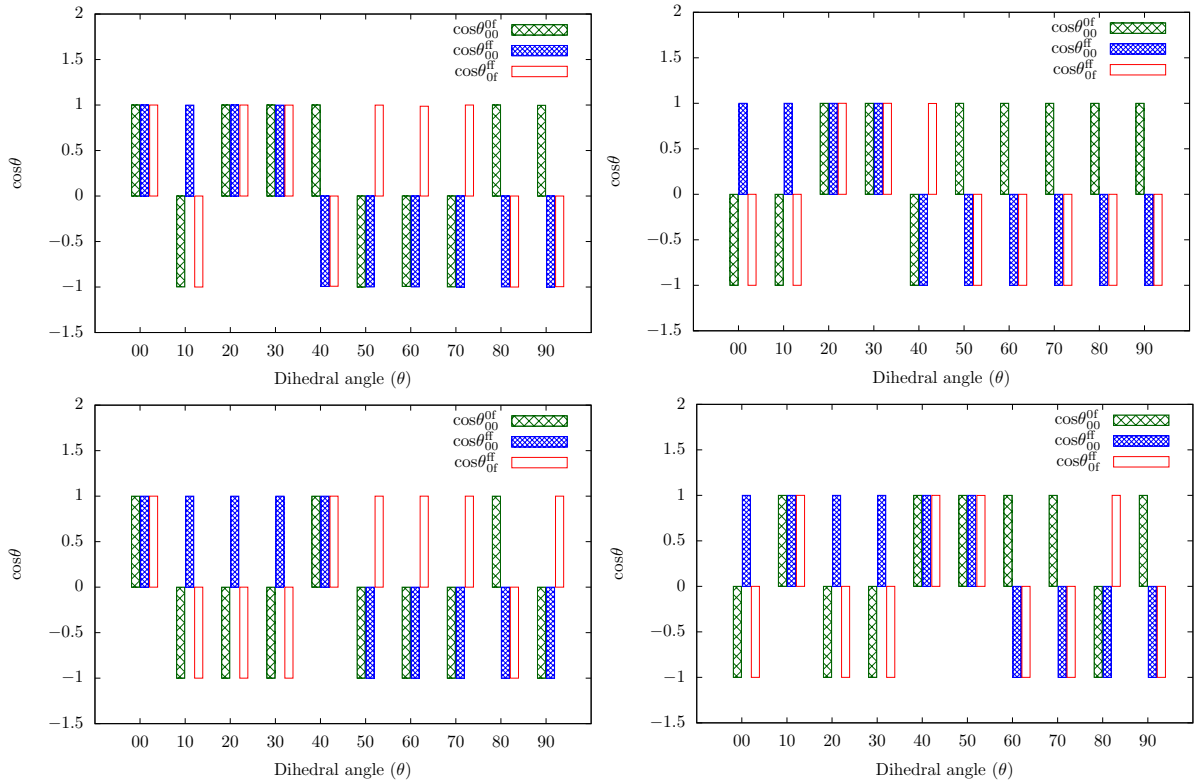

Figure S2: Variation of different cosθ terms involved in 2SM in vacuum (top left panel), in C_6H_{12} (top right panel), in CH_2Cl_2 (bottom left panel) and in CH_3CN (bottom right panel).

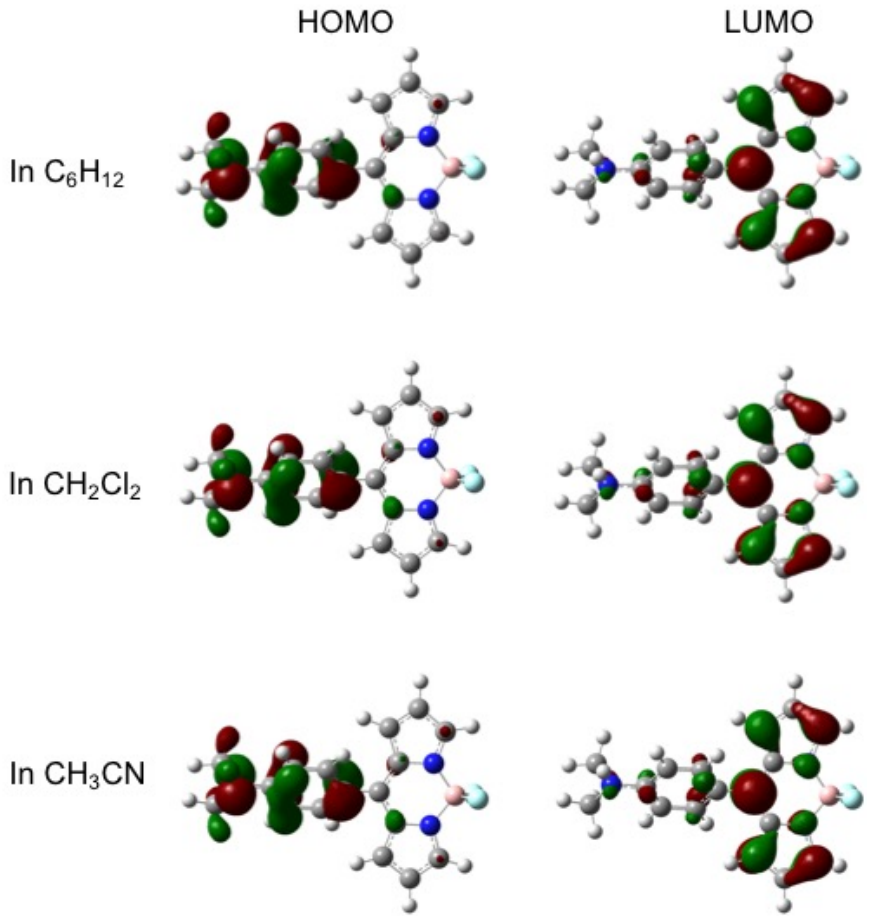

Figure S3: Orbital pictures involved in most intense two-photon absorption in molecule 3 in three solvents.

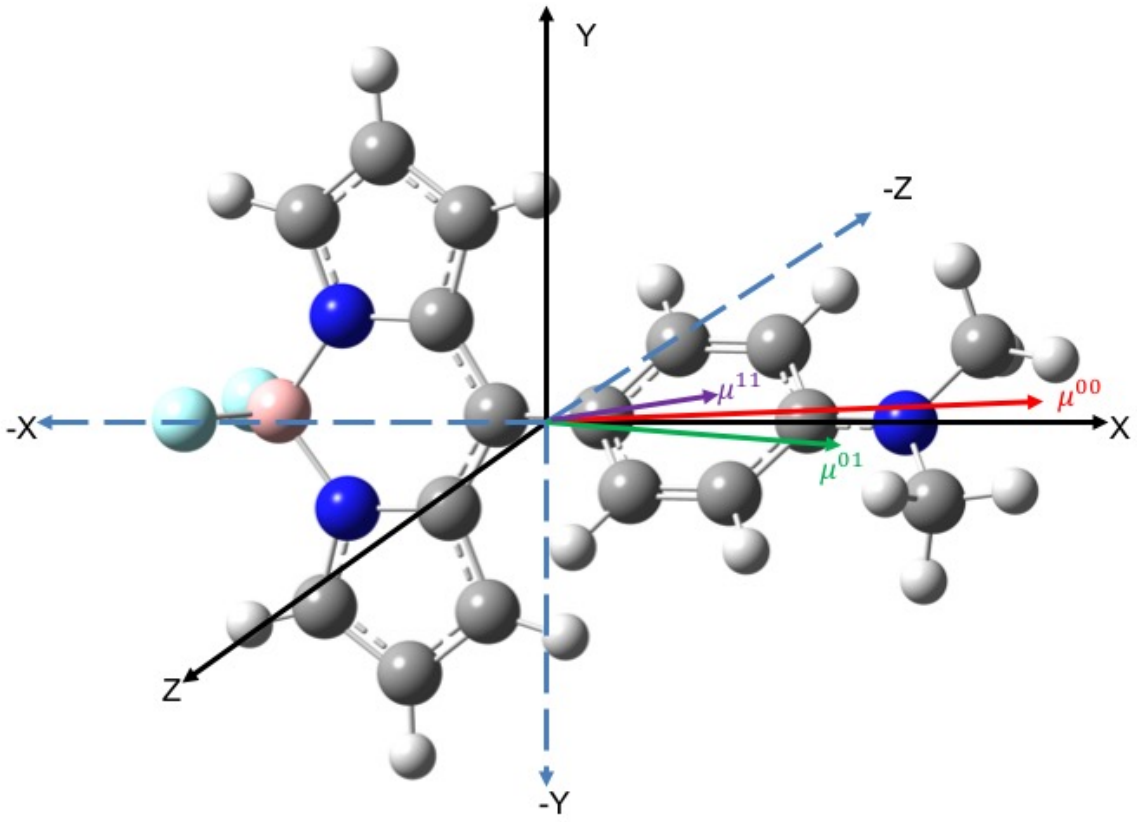

Figure S4: Relative orientation of ground-state dipole moment, excited state dipole moment and the corresponding transition moment vectors in molecule 3 in CH_2Cl_2 solvent.

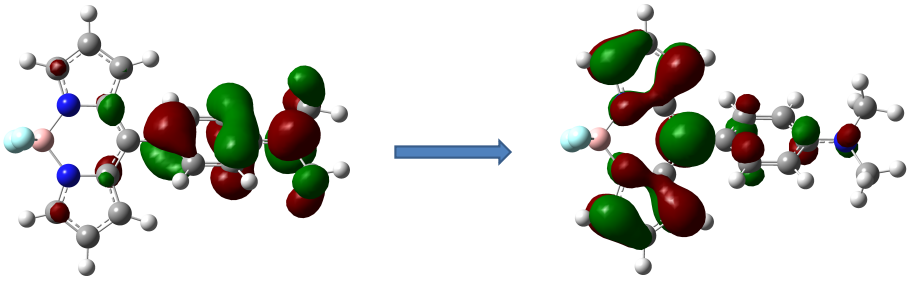

Figure S5: Natural transition orbitals in molecule 3 in CH_2Cl_2 solvent.

Table S1: Cartesian coordinates of ground state geometry of molecule 3

	CH_2Cl_2		
Atoms	X	Y	Z
H	0.198484	2.840953	0.417100
H	-1.989098	4.411625	0.540039
H	0.198677	-2.840639	-0.418309
H	3.525829	-1.564633	1.491554
H	3.526082	1.564699	-1.491373
H	-1.988803	-4.411415	-0.541957
H	-4.118875	2.751477	0.262134
H	1.107074	-1.561406	1.472725
H	-4.118692	-2.751539	-0.263275
H	1.107333	1.561477	-1.472964
H	6.916809	0.793714	-0.680601
H	5.602678	1.972301	-0.597195
H	5.640865	0.768496	-1.903975
H	6.916650	-0.793680	0.681482
H	5.602685	-1.972407	0.596907
H	5.640247	-0.769318	1.904362
B	-3.587561	-0.000107	0.000554
C	0.902965	0.000061	-0.000109
C	-0.560848	0.000051	-0.000192
C	-1.275613	-1.210176	-0.104507
C	-1.275688	1.210243	0.104004
C	-0.830769	2.532658	0.312995
C	-0.830600	-2.532478	-0.314024
C	-1.957700	3.342963	0.385961
C	3.015428	-0.881889	0.825389
C	3.015569	0.881993	-0.825256
C	-1.957474	-3.342825	-0.387367
C	3.753559	0.000075	0.000157
C	-3.066904	2.502003	0.239969
C	-3.066738	-2.502001	-0.241022
C	1.634050	-0.884926	0.808595
C	1.634188	0.885031	-0.808704
C	5.849105	0.932303	-0.840006
C	5.848903	-0.932506	0.840388
N	-2.665960	1.233164	0.073238
N	-2.665879	-1.233207	-0.073771
N	5.118593	0.000113	0.000342
F	-4.405923	-0.062673	1.139274
F	-4.408078	0.062325	-1.136576

Table S2: Cartesian coordinates of ground state geometry of molecule 3

	CH_3CN		
Atoms	X	Y	Z
H	0.19676900	-2.84280100	-0.41913000
H	-1.99128700	-4.41167100	-0.53937600
H	0.19728200	2.84222600	0.42047500
H	3.52629700	1.58056500	-1.47544500
H	3.52668500	-1.58070400	1.47503300
H	-1.99051000	4.41142700	0.54171200
H	-4.11988500	-2.75171000	-0.25940800
H	1.10873600	1.57716100	-1.45690000
H	-4.11941100	2.75197300	0.26103000
H	1.10911900	-1.57732500	1.45707800
H	6.91687600	-0.80080300	0.67169400
H	5.60279900	-1.97871300	0.57557500
H	5.64090700	-0.78931000	1.89535600
H	6.91687700	0.80075100	-0.67216900
H	5.60292000	1.97876100	-0.57519800
H	5.64080800	0.79013900	-1.89568700
B	-3.58473500	0.00020000	-0.00064000
C	0.90325100	-0.00013700	0.00005300
C	-0.55910800	-0.00010700	0.00018200
C	-1.27506700	1.21052700	0.10372300
C	-1.27526200	-1.21065300	-0.10316600
C	-0.83180800	-2.53286800	-0.31354400
C	-0.83136300	2.53255800	0.31475500
C	-1.95962000	-3.34301800	-0.38526100
C	3.01595500	0.89095000	-0.81639900
C	3.01616200	-0.89112500	0.81608000
C	-1.95902900	3.34285800	0.38698500
C	3.75457500	-0.00010000	-0.00025900
C	-3.06788600	-2.50219700	-0.23789800
C	-3.06745600	2.50229200	0.23931400
C	1.63503300	0.89394600	-0.79926000
C	1.63523700	-0.89415200	0.79925500
C	5.84942200	-0.94168500	0.82990200
C	5.84942100	0.94185300	-0.83016500
N	-2.66580400	-1.23274400	-0.07105200
N	-2.66560100	1.23285400	0.07187000
N	5.11827800	-0.00015900	-0.00040200
F	-4.40662200	0.06068500	-1.13943500
F	-4.40939600	-0.06004800	1.13608800

Table S3: Cartesian coordinates of ground state geometry of molecule 3

	C_6H_{12}		
Atoms	X	Y	Z
H	0.20274500	2.83722800	0.41122900
H	-1.98327200	4.41195300	0.53848600
H	0.20291700	-2.83696200	-0.41220100
H	3.52399700	-1.51946400	1.53551000
H	3.52421700	1.51952200	-1.53533700
H	-1.98300800	-4.41178000	-0.54005900
H	-4.11661800	2.74922200	0.26813800
H	1.10189700	-1.51594000	1.51632000
H	-4.11645500	-2.74928000	-0.26907900
H	1.10211700	1.51599300	-1.51650300
H	6.91630700	0.77325100	-0.70572400
H	5.60256700	1.95377700	-0.65503400
H	5.63906600	0.71220100	-1.92624300
H	6.91620500	-0.77319900	0.70637100
H	5.60261400	-1.95388200	0.65470400
H	5.63862700	-0.71294100	1.92654500
B	-3.59684800	-0.00009400	0.00045400
C	0.90181900	0.00005300	-0.00007800
C	-0.56618900	0.00004400	-0.00014500
C	-1.27698500	-1.20930200	-0.10673200
C	-1.27705200	1.20935800	0.10633700
C	-0.82813100	2.53267000	0.31107300
C	-0.82797900	-2.53251700	-0.31190800
C	-1.95267600	3.34309100	0.38585500
C	3.01360800	-0.85589600	0.85011300
C	3.01372900	0.85598900	-0.84997900
C	-1.95247500	-3.34297600	-0.38700900
C	3.75020100	0.00007000	0.00014400
C	-3.06441900	2.50107200	0.24442700
C	-3.06427100	-2.50107400	-0.24529300
C	1.63093500	-0.85859100	0.83459600
C	1.63105300	0.85867700	-0.83466700
C	5.84771300	0.90618900	-0.86693500
C	5.84758200	-0.90636500	0.86720300
N	-2.66642300	1.23431900	0.07917500
N	-2.66635100	-1.23435500	-0.07960900
N	5.11956200	0.00011600	0.00029100
F	-4.40222800	-0.06780400	1.13984900
F	-4.40399200	0.06750000	-1.13767200

Table S4: Vacuum phase OPA data for molecules 1–7. The last column represent the involved orbitals, their weights and their contributions.

Molecules	Ex. St. (i)	ω_{0i} (a.u.)	δ^{1P} (a.u.)	μ^{0i} (a.u.)	Orbitals, weights & contributions	Λ
1	1	0.109	0.531	2.698	H-L 0.390 0.284	0.6973
	2	0.143	0.046	0.691	H-1–L 0.447 0.284	0.6250
	3	0.153	0.042	0.641	H-2–L 0.453 0.302	0.6571
	4	0.170	0.000	0.014	H-3–L 0.481 0.090	0.1922
	5	0.178	0.000	0.032	H–L+2 0.457 0.084	0.1850
2	1	0.112	0.438	2.421	H–L 0.382 0.269	0.6769
	2	0.145	0.071	0.862	H-1–L 0.430 0.283	0.6433
	3	0.154	0.007	0.266	H-3–L 0.325 0.205	0.5954
	4	0.156	0.252	1.556	H-2–L 0.330 0.175	0.5514
	5	0.170	0.004	0.215	H-4–L 0.456 0.163	0.3760
3	1	0.113	0.419	2.367	H-1–L 0.388 0.267	0.6624
	2	0.117	0.341	2.090	H–L 0.451 0.185	0.4191
	3	0.146	0.060	0.793	H-2–L 0.438 0.283	0.6356
	4	0.156	0.048	0.681	H-3–L 0.454 0.283	0.6132
	5	0.166	0.017	0.441	H-4–L 0.211 0.069	0.3984
					H–L+3 0.148 0.068	
					H–L+4 0.108 0.047	
4	1	0.111	0.423	2.406	H–L 0.368 0.247	0.6351
	2	0.143	0.058	0.783	H-1–L 0.406 0.250	0.5902
	3	0.144	0.000	0.047	H-5-L+1 0.299 0.160	0.4962
					H-5-L 0.085 0.033	
	4	0.152	0.021	0.454	H-2-L 0.425 0.250	0.5681
	5	0.154	0.037	0.616	H–L+1 0.427 0.140	0.3417
5	1	0.110	0.522	2.674	H–L 0.391 0.284	0.6953
	2	0.128	0.000	0.003	H-1–L 0.471 0.062	0.1366
	3	0.143	0.043	0.670	H-2–L 0.446 0.283	0.6220
	4	0.154	0.040	0.621	H-3–L 0.453 0.303	0.6573
	5	0.169	0.033	0.545	H-1–L+5 0.425 0.249	0.5407
6	1	0.109	0.533	2.708	H–L 0.389 0.284	0.7007
	2	0.131	0.000	0.031	H–L+1 0.473 0.047	0.1020
	3	0.142	0.046	0.697	H-1–L 0.447 0.285	0.6271
	4	0.152	0.040	0.625	H-2–L 0.452 0.301	0.6551
	5	0.174	0.033	0.533	H–L+2 0.489 0.087	0.1815
7	1	0.113	0.429	2.389	H–L 0.387 0.268	0.6660
	2	0.126	0.283	1.832	H-1–L 0.455 0.197	0.4333
	3	0.146	0.064	0.820	H-2–L 0.438 0.284	0.6374
	4	0.155	0.049	0.687	H-3–L 0.453 0.284	0.6161
	5	0.170	0.007	0.271	H-4–L 0.295 0.092	0.3973
					H-1–L+2 0.156 0.091	

Table S5: vacuum phase OPA data for molecules 8–14. The last column represent the involved orbitals, their weights and their contributions.

Molecules	Ex. St. (i)	ω_{0i} (a.u.)	δ^{1P} (a.u.)	μ^{0i} (a.u.)	Orbitals, weights & contributions	Λ
8	1	0.109	0.528	2.690	H–L 0.391 0.284	0.6974
	2	0.137	0.000	0.021	H-1–L 0.476 0.070	0.1556
	3	0.143	0.045	0.684	H-2–L 0.447 0.283	0.6242
	4	0.154	0.040	0.628	H-3–L 0.453 0.302	0.6574
	5	0.175	0.024	0.456	H-1–L+2 0.390 0.234	0.5179
9	1	0.111	0.432	2.422	H–L 0.378 0.265	0.6128
	2	0.143	0.071	0.865	H-1–L 0.434 0.279	0.5406
	3	0.152	0.015	0.390	H-3–L 0.446 0.278	0.1691
	4	0.161	0.367	1.846	H-2–L 0.447 0.245	0.7568
	5	0.172	0.016	0.399	H–L+1 0.446 0.123	0.7592
10	1	0.109	0.532	2.705	H–L 0.389 0.284	0.6546
	2	0.142	0.047	0.701	H-1–L 0.447 0.285	0.1798
	3	0.150	0.000	0.029	H–L+1 0.485 0.069	0.1824
	4	0.152	0.041	0.636	H-2–L 0.452 0.301	0.1535
	5	0.174	0.033	0.534	H–L+2 0.488 0.086	0.7658
11	1	0.113	0.434	2.411	H–L 0.383 0.269	0.6733
	2	0.145	0.069	0.851	H-2–L 0.430 0.282	0.6415
	3	0.148	0.214	1.474	H-1–L 0.449 0.222	0.4937
	4	0.155	0.080	0.880	H-3–L 0.441 0.278	0.6168
	5	0.169	0.003	0.198	H-4–L 0.450 0.163	0.3834
12	1	0.109	0.528	2.691	H–L 0.391 0.284	0.6975
	2	0.143	0.045	0.686	H-1–L 0.446 0.283	0.6245
	3	0.154	0.042	0.641	H-2–L 0.453 0.302	0.6569
	4	0.162	0.000	0.001	H-3–L 0.479 0.084	0.1807
	5	0.181	0.000	0.036	H–L+2 0.403 0.068	0.1693
13	1	0.111	0.428	2.412	H–L 0.377 0.261	0.6617
	2	0.138	0.000	0.041	H-4–L+1 0.323 0.142	0.3690
	3	0.144	0.067	0.843	H-1–L 0.424 0.274	0.6279
	4	0.152	0.011	0.323	H-3–L 0.442 0.273	0.6045
	5	0.160	0.393	1.922	H-2–L 0.448 0.263	0.5784
14	1	0.109	0.531	2.702	H–L 0.389 0.284	0.6972
	2	0.142	0.046	0.695	H-1–L 0.447 0.284	0.6262
	3	0.143	0.000	0.053	H–L+1 0.479 0.058	0.1264
	4	0.153	0.040	0.628	H-2–L 0.452 0.301	0.6550
	5	0.179	0.032	0.517	H–L+2 0.484 0.088	0.1866

Table S6: vacuum phase TPA data for molecules 1–7 obtained from quadratic response theory, two- and three-state model calculations.

Molecules	Excited states	$\delta^{2P}_{Resp.}$ (a.u.)	δ^{2P}_{2SM} (a.u.)	δ^{2P}_{3SM} (a.u.)
1	1	155.0	47.892	59.0553 (3)
	2	198.0	0.267	65.3676 (3)
	3	0.197	3.003	2.9993 (5)
	4	2.900	0.411	1.9393 (1)
	5	0.662	0.892	0.7956 (3)
2	1	217.0	90.412	161.0448 (4)
	2	67.60	8.820	32.3049 (4)
	3	659.0	2.250	355.7575 (1)
	4	1140	1644.6	1648.5986 (5)
	5	88.60	29.267	45.1965 (1)
3	1	452.0	136.082	137.6860 (5)
	2	15300	21405.679	20400.409 (1)
	3	57.50	15.656	37.3414 (2)
	4	143.0	43.155	283.3685 (3)
	5	5.980	27.356	13.9539 (2)
4	1	307.0	215.45	232.9139 (2)
	2	3.970	29.370	0.5210 (5)
	3	0.174	0.240	0.2250 (1)
	4	198.0	18.443	266.2485 (2)
	5	1630	734.99	799.4772 (1)
5	1	179.0	56.302	67.6180 (4)
	2	0.911	0.071	0.5081 (1)
	3	215.0	0.528	42.8998 (4)
	4	0.544	4.221	4.1587 (5)
	5	6.940	14.618	14.6128 (1)
6	1	160.0	50.451	62.0341 (4)
	2	4.310	3.370	4.2948 (5)
	3	190.0	0.549	44.4979 (4)
	4	1.060	3.615	1.6618 (5)
	5	484.0	872.59	794.5461 (1)
7	1	351.0	112.655	213.3230 (2)
	2	7890.0	11364.5	10634.4478 (1)
	3	57.900	13.339	30.9672 (2)
	4	155.00	34.925	303.2511 (3)
	5	5.990	14.709	4.5657 (3)

Table S7: vacuum phase TPA data for molecules 8–14 obtained from quadratic response theory, two- and three-state model calculations.

Molecules	Excited states	$\delta^{2P}_{Resp.}$ (a.u.)	δ^{2P}_{2SM} (a.u.)	δ^{2P}_{3SM} (a.u.)
8	1	168.0	52.255	63.3981 (4)
	2	2.490	2.273	2.3925 (4)
	3	207.0	0.534	45.6911 (4)
	4	0.128	3.591	3.5607 (5)
	5	9.050	2.014	2.0988 (4)
9	1	271.00	137.0922	251.2609 (10)
	2	41.100	17.0057	47.5144 (1)
	3	248.00	10.3182	417.8036 (2)
	4	1940.0	5397.9685	2572.9906 (9)
	5	2060.0	151.1917	4019.7869 (1)
10	1	163.00	51.5175	53.2357 (5)
	2	192.00	0.5942	69.0204 (4)
	3	1.92	1.4627	2.0968 (10)
	4	0.76	3.9103	1.8400 (5)
	5	499.00	900.8856	835.7074 (4)
11	1	254.00	92.603	146.6651 (4)
	2	67.900	10.295	40.1996 (3)
	3	2900.0	4204.05	3883.4643 (1)
	4	207.00	30.055	312.1608 (2)
	5	71.400	25.794	36.3587 (1)
12	1	164.00	50.939	62.3500 (3)
	2	202.00	0.340	48.4464 (3)
	3	0.0873	3.496	3.4905 (5)
	4	1.9900	0.001	0.9740 (1)
	5	1.3500	1.192	1.2179 (1)
13	1	293.00	163.547	231.0086 (5)
	2	0.1060	0.242	0.1367 (4)
	3	33.400	18.222	17.8891 (2)
	4	242.00	7.245	197.3966 (5)
	5	1210.0	4334.78	3875.6902 (1)
14	1	164.00	51.385	62.9732 (4)
	2	195.00	0.5263	44.9126 (4)
	3	13.300	15.566	14.1251 (1)
	4	0.4220	3.736	2.2559 (5)
	5	475.00	769.34	722.6227 (4)

Table S8: OPA and TPA rotation data for molecule-3 in vacuum phase: variation of excitation energy (eV) and TP strength (10^3 a.u.) with the dihedral angle (in degree) between the two parts of the molecule.

θ	ω_{0i}	μ^{0i}	δ_i^{1P}	$\delta_{i,Res}^{2P}$	$\delta_{i,2SM}^{2P}$
0°	2.92	2.62	0.49	12.200	13.392
10°	2.93	2.59	0.48	11.100	13.893
20°	2.99	2.54	0.47	13.400	15.603
30°	3.07	2.45	0.45	14.400	17.990
40°	3.12	2.28	0.40	15.300	20.277
50°	3.12	2.00	0.31	15.200	20.896
60°	3.09	1.62	0.19	12.800	19.289
70°	3.04	1.11	0.09	7.900	11.097
80°	2.99	0.53	0.02	2.190	5.051
90°	2.98	0.08	0.00	0.056	0.077

Table S9: OPA and TPA rotation data for molecule 3 in CH_3CN solvent: variation of excitation energy (eV) and TP strength (10^3 a.u.) with the dihedral angle (in degree) between the two parts of the molecule.

θ	ω_{0i}	μ^{0i}	δ_i^{1P}	$\delta_{i,Res}^{2P}$	$\delta_{i,2SM}^{2P}$
0°	2.60	3.24	0.67	24.600	27.390
10°	2.60	3.20	0.65	25.600	28.824
20°	2.63	3.12	0.63	28.400	32.975
30°	2.68	2.98	0.58	31.900	38.675
40°	2.70	2.77	0.51	35.600	44.684
50°	2.69	2.42	0.38	36.300	46.525
60°	2.64	1.94	0.24	32.100	41.480
70°	2.58	1.35	0.11	20.500	26.493
80°	2.54	0.65	0.03	5.720	7.404
90°	2.53	0.11	0.00	0.188	0.239

Table S10: OPA and TPA rotation data for molecule 3 in CH_2Cl_2 solvent: variation of excitation energy (eV) and TP strength (10^3 a.u.) with the dihedral angle (in degree) between the two parts of the molecule.

θ	ω_{0i}	μ^{0i}	δ_i^{1P}	$\delta_{i,Res}^{2P}$	$\delta_{i,2SM}^{2P}$
0°	2.61	3.24	0.67	27.300	30.827
10°	2.62	3.20	0.66	28.400	32.314
20°	2.65	3.12	0.63	30.900	36.351
30°	2.71	2.99	0.59	34.100	41.824
41°	2.74	2.73	0.50	37.000	47.219
50°	2.73	2.42	0.39	37.200	48.426
60°	2.69	1.95	0.25	32.200	42.337
70°	2.64	1.35	0.12	20.200	26.577
80°	2.59	0.65	0.03	5.610	7.358
90°	2.58	0.11	0.00	0.176	0.225

Table S11: OPA and TPA rotation data for molecule 3 in C_6H_{12} solvent: variation of excitation energy (eV) and TP strength (10^3 a.u.) with the dihedral angle (in degree) between the two parts of the molecule.

θ	ω_{0i}	μ^{0i}	δ_i^{1P}	$\delta_{i,Res}^{2P}$	$\delta_{i,2SM}^{2P}$
0°	2.73	3.08	0.63	30.038	27.755
10°	2.73	3.04	0.62	31.200	28.889
20°	2.79	2.97	0.60	34.133	31.732
30°	2.85	2.85	0.57	38.222	35.720
40°	2.90	2.64	0.49	41.101	38.673
50°	2.91	2.32	0.38	41.841	39.606
60°	2.88	1.87	0.25	35.487	33.805
70°	2.83	1.30	0.12	21.640	20.722
80°	2.79	0.62	0.03	5.904	5.669
90°	2.78	0.10	0.00	0.152	0.149

Table S12: Contribution of different optical channels (involved in 2SM) to TP activity of molecule 3, in gas phase

θ	vacuum		
	δ_{00}	$2 \times \delta_{0f}$	δ_{ff}
0°	29.665	-19.468	3.194
10°	28.630	-17.375	2.637
20°	26.304	-12.090	1.390
30°	22.734	-5.022	0.278
40°	18.195	2.025	0.057
50°	13.084	6.901	0.910
60°	8.002	8.842	2.445
70°	3.677	5.422	1.999
80°	0.833	2.436	1.781
90°	0.020	0.039	0.019

Table S13: Contribution of different optical channels (involved in 2SM) to TP activity of molecule 3

θ	C_6H_{12}			CH_3CN			CH_2Cl_2		
	δ_{00}	$2 \times \delta_{0f}$	δ_{ff}	δ_{00}	$2 \times \delta_{0f}$	δ_{ff}	δ_{00}	$2 \times \delta_{0f}$	δ_{ff}
0°	64.593	-41.089	6.534	122.093	-128.529	33.826	109.180	-102.330	23.977
10°	62.199	-36.292	5.294	117.904	-119.215	30.135	104.300	-92.490	20.504
20°	56.338	-24.971	2.767	105.974	-93.719	20.720	94.967	-72.424	13.808
30°	48.008	-10.343	0.557	89.003	-60.665	10.338	79.736	-43.975	6.063
40°	37.155	3.846	0.099	69.718	-27.806	2.773	84.831	-6.398	0.142
50°	26.706	13.442	1.691	48.329	-1.821	0.017	43.444	4.847	0.135
60°	16.145	15.582	3.760	28.920	11.431	1.129	26.031	14.333	1.973
70°	7.366	10.518	3.755	13.043	11.092	2.358	11.767	11.834	2.975
80°	1.654	2.942	1.308	2.881	3.476	1.048	2.614	3.543	1.200
90°	0.040	0.076	0.035	0.087	0.115	0.038	0.075	0.110	0.040