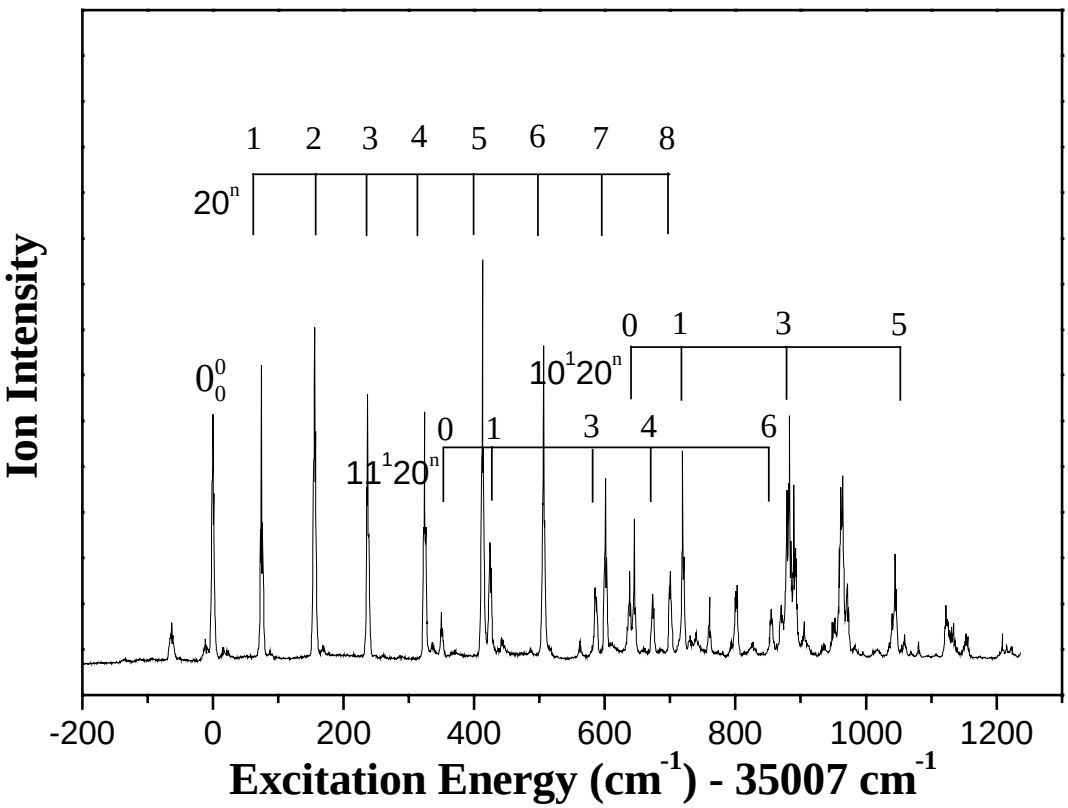
Supporting information:

A: Two-color two-photon resonantly enhanced multiphoton spectrum of TTD:



B. Geometry of TTD in the S_1 state calculated at the CIS level using the 6-31G basis set.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.394525	-0.749781	-0.000069
2	6	0	-2.394454	0.749863	0.000070
3	1	0	-2.786152	-1.211093	-0.891657
4	1	0	-2.786758	-1.211249	0.891174
5	1	0	-2.786874	1.211213	-0.891167
6	1	0	-2.786277	1.211055	0.891646
7	7	0	-0.651577	-1.495260	0.000340
8	7	0	-0.651553	1.495206	-0.000342
9	6	0	0.052991	-1.243848	1.257743
10	1	0	-0.692206	-1.255477	2.039553
11	1	0	0.742426	-2.061246	1.445230
12	7	0	0.800587	0.000297	1.340801
13	6	0	0.053350	1.244029	-1.257619
14	1	0	-0.691494	1.256337	-2.039743
15	1	0	0.743162	2.061303	-1.444278
16	6	0	0.053636	1.244748	1.256927
17	1	0	0.743701	2.061985	1.442823
18	1	0	-0.690998	1.257799	2.039238
19	7	0	0.800589	-0.000300	-1.340799
20	6	0	2.138118	-0.000191	-0.780211
21	6	0	2.138118	-0.000259	0.780213
22	1	0	2.662612	0.869890	-1.156875
23	1	0	2.662795	-0.870139	-1.156925
24	1	0	2.663141	0.869473	1.156954
25	1	0	2.662263	-0.870557	1.156852
26	6	0	0.053280	-1.244566	-1.257052
27	1	0	-0.691707	-1.256935	-2.039052
28	1	0	0.742967	-2.061928	-1.443777

C. Geometry of TTD in the D_0 state with a D_{2d} symmetry calculated using the Becke 3LYP functional with the 6-31+G(d) basis set.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.064600	-0.015660	0.805575
2	6	0	-2.064607	0.015635	-0.805575
3	1	0	-2.608391	-0.905119	1.136158
4	1	0	-2.594490	0.868236	1.171545
5	1	0	-2.594477	-0.868276	-1.171539
6	1	0	-2.608413	0.905089	-1.136148
7	7	0	-0.750881	-0.036169	1.385796
8	7	0	-0.750889	0.036166	-1.385794
9	6	0	0.004054	1.221354	1.291433
10	1	0	-0.708689	2.043661	1.398280
11	1	0	0.722832	1.273284	2.113813
12	7	0	0.750878	1.385855	0.036174
13	6	0	0.004061	-1.221346	-1.291430
14	1	0	-0.708663	-2.043665	-1.398306
15	1	0	0.722849	-1.273253	-2.113803
16	6	0	-0.004066	1.291416	-1.221353
17	1	0	0.708707	1.398175	-2.043645
18	1	0	-0.722811	2.113819	-1.273365
19	7	0	0.750887	-1.385857	-0.036174
20	6	0	2.064585	-0.805583	-0.015639
21	6	0	2.064580	0.805590	0.015623
22	1	0	2.608455	-1.136174	-0.905046
23	1	0	2.594427	-1.171510	0.868305
24	1	0	2.594394	1.171519	-0.868337
25	1	0	2.608468	1.136191	0.905016
26	6	0	-0.004037	-1.291405	1.221366
27	1	0	-0.722751	-2.113832	1.273422
28	1	0	0.708764	-1.398127	2.043637

Average bond angle for the NR_3 group: 116º

D. Geometry of TTD in the D_0 state with a C_{2v} symmetry calculated using the Becke 3LYP functional with the 6-31+G(d) basis set.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.268195	1.181464	-0.004063
2	7	0	0.000000	1.141155	0.754591
3	6	0	0.000000	0.771391	2.199345
4	6	0	0.000000	-0.771391	2.199345
5	7	0	0.000000	-1.141155	0.754591
6	6	0	1.268195	-1.181464	-0.004063
7	6	0	-1.268195	-1.181464	-0.004063
8	6	0	-1.268195	1.181464	-0.004063
9	1	0	2.080751	1.262984	0.724350
10	7	0	1.456058	0.000000	-0.825496
11	6	0	0.787659	0.000000	-2.134755
12	1	0	1.276335	-2.071103	-0.642403
13	1	0	-1.276335	2.071103	-0.642403
14	1	0	-0.881783	-1.206539	2.676722
15	1	0	0.881783	-1.206539	2.676722
16	1	0	-0.881783	1.206539	2.676722
17	1	0	0.881783	1.206539	2.676722
18	6	0	-0.787659	0.000000	-2.134755
19	1	0	-1.276335	-2.071103	-0.642403
20	7	0	-1.456058	0.000000	-0.825496
21	1	0	1.276335	2.071103	-0.642403
22	1	0	2.080751	-1.262984	0.724350
23	1	0	-2.080751	-1.262984	0.724350
24	1	0	-2.080751	1.262984	0.724350
25	1	0	1.158497	0.873691	-2.679892
26	1	0	-1.158497	0.873691	-2.679892
27	1	0	-1.158497	-0.873691	-2.679892
28	1	0	1.158497	-0.873691	-2.679892

Average bond angles for the two nonequivalent NR_3 groups: 114º and 120º.