Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Supporting Information File

Photochemical formation of thiirene and thioketene in 1,2,3-thiadiazoles with phenyl substituents studied by time-resolved spectroscopy.

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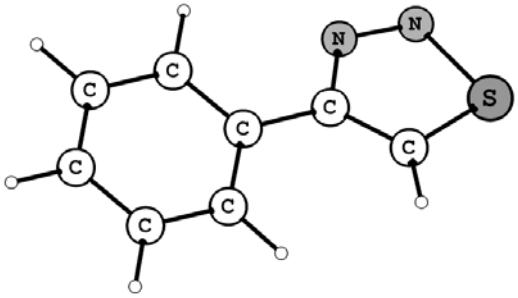
Table S1. Optimized structure of PT at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)

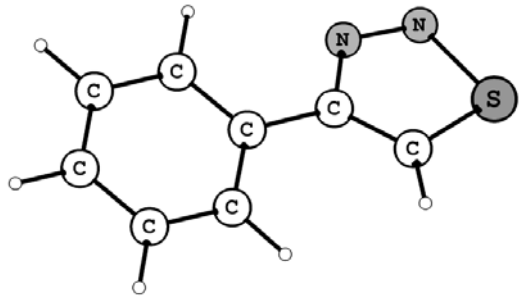


Energy = -816.1351794 Hartree

C	-0.154231000	0.090527000	0.855616000
C	0.806528000	-0.274272000	-0.065627000
S	-0.922251000	1.525123000	0.355826000
H	-0.429904000	-0.426503000	1.764190000
N	0.070265000	1.596336000	-1.087869000
N	0.872462000	0.613285000	-1.124623000
C	1.704226000	-1.443863000	-0.035795000
C	1.835535000	-2.233854000	1.119323000
C	2.448543000	-1.789303000	-1.177478000
C	2.680100000	-3.343524000	1.130857000
H	1.286885000	-1.977485000	2.021797000
C	3.294173000	-2.898977000	-1.162082000
H	2.356922000	-1.182355000	-2.072046000
C	3.413227000	-3.682068000	-0.010648000
H	2.770093000	-3.940406000	2.034778000
H	3.860820000	-3.152133000	-2.054455000
H	4.072667000	-4.545913000	-0.000715000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
22	4	750	10.5	1226	19
97	0.1	769	1.6	1296	10.8
144	1.7	822	0.1	1319	0.2
254	0	864	28.4	1360	43.8
307	0.5	899	2.4	1427	8.9
396	0	904	25.4	1455	36.8
407	1.4	946	0.2	1497	2
458	22.9	967	0.2	1568	0.8
461	8.1	976	0.2	1592	3.2
518	6.3	1007	4.4	3059	3
608	0	1026	5.8	3066	3.3
642	4.3	1067	5	3075	29.6
669	6.2	1147	0	3085	21.9
674	25.3	1168	1.4	3101	2.4
741	85.7	1175	0	3156	3.1

Table S2. TD DFT of PT at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

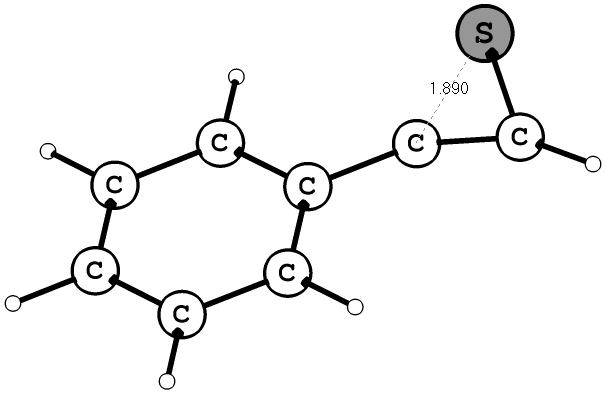


Energy = -816.1351794 Hartree

Wavelength (nm)	*f*
303.1	0.0431
302.2	0.025
270.2	0.0035
251.0	0.0821
248.2	0.1509
244.2	0.1696
237.8	0.0022
227.1	0.0104
214.6	0.0012
210.9	0.0457

C	-0.154231000	0.090527000	0.855616000
C	0.806528000	-0.274272000	-0.065627000
S	-0.922251000	1.525123000	0.355826000
H	-0.429904000	-0.426503000	1.764190000
N	0.070265000	1.596336000	-1.087869000
N	0.872462000	0.613285000	-1.124623000
C	1.704226000	-1.443863000	-0.035795000
C	1.835535000	-2.233854000	1.119323000
C	2.448543000	-1.789303000	-1.177478000
C	2.680100000	-3.343524000	1.130857000
H	1.286885000	-1.977485000	2.021797000
C	3.294173000	-2.898977000	-1.162082000
H	2.356922000	-1.182355000	-2.072046000
C	3.413227000	-3.682068000	-0.010648000
H	2.770093000	-3.940406000	2.034778000
H	3.860820000	-3.152133000	-2.054455000
H	4.072667000	-4.545913000	-0.000715000

Table S3. Optimized structure of phenylthiirene at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)

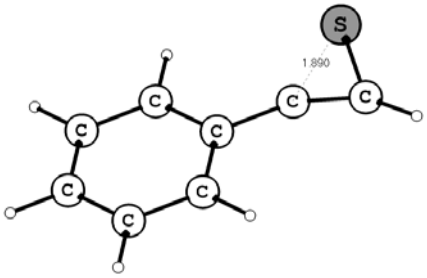


Energy = -706.5778694 Hartree

S	2.775547000	-0.610511000	0.004495000
C	2.266737000	1.158884000	0.003278000
H	2.756532000	2.119735000	0.003253000
C	1.201547000	0.435137000	0.002762000
C	-0.213444000	0.194822000	0.001736000
C	-0.711650000	-1.120426000	0.002024000
C	-1.118126000	1.278824000	0.000430000
C	-2.088340000	-1.347889000	0.001032000
H	-0.011866000	-1.950782000	0.003024000
C	-2.489117000	1.041522000	-0.000553000
H	-0.736777000	2.296327000	0.000199000
C	-2.979364000	-0.271588000	-0.000255000
H	-2.464743000	-2.367325000	0.001265000
H	-3.180152000	1.880412000	-0.001557000
H	-4.051173000	-0.451094000	-0.001028000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
65	2.1	739	42.9	1284	2.9
118	0.4	763	1.9	1313	1.7
121	2.8	819	0.2	1427	11.2
262	1.2	894	2.3	1469	10.6
331	4.6	915	12.4	1557	3.6
399	0	943	0.1	1582	3.7
458	0	965	0	1782	15.1
496	0.1	973	0.1	3062	1
536	0.2	1009	3.7	3069	2.5
604	2.6	1067	6	3078	18
624	34.2	1146	0	3085	22.4
657	46.2	1157	0.1	3092	7.1
672	51	1172	0.1	3191	24.2

Table S4. TD DFT of phenylthiirene at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.



Energy = -706.5778694 Hartree

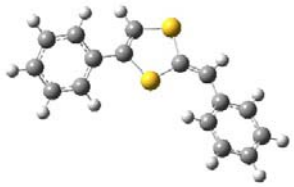
Wavelength (nm)	*f*
446.9	0.0817
354.0	0.0000
329.4	0.0106
288.4	0.0061
268.2	0.0061
251.0	0.0303
245.4	0.0085
244.0	0.0041
233.8	0.0017
233.5	0.3277

S	2.775547000	-0.610511000	0.004495000
C	2.266737000	1.158884000	0.003278000
H	2.756532000	2.119735000	0.003253000
C	1.201547000	0.435137000	0.002762000
C	-0.213444000	0.194822000	0.001736000
C	-0.711650000	-1.120426000	0.002024000
C	-1.118126000	1.278824000	0.000430000
C	-2.088340000	-1.347889000	0.001032000
H	-0.011866000	-1.950782000	0.003024000
C	-2.489117000	1.041522000	-0.000553000
H	-0.736777000	2.296327000	0.000199000
C	-2.979364000	-0.271588000	-0.000255000
H	-2.464743000	-2.367325000	0.001265000
H	-3.180152000	1.880412000	-0.001557000
H	-4.051173000	-0.451094000	-0.001028000

TD DFT B3LYP/6-311+G(d,p) using PCM model to include presence of solvent (acetonitrile):

Wavelength (nm)	*f*
402.3	0.1271
336.6	0
300.3	0.0098
278.0	0.0113
251.8	0.0526
250.8	0.0191
237.5	0.3009
228.4	0.117
225.3	0.0155
218.6	0.0002

Table S5. Optimized structure of 2-benzylidene-4-phenyl-1,3-dithiole (*cis* form) at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)



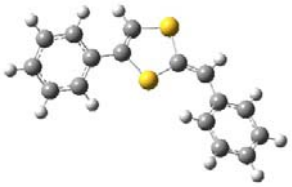
Energy = -1413.3057671. Hartree

C	1.611184000	1.973169000	0.137449000
C	1.706055000	0.633903000	0.021190000
S	0.031288000	2.722230000	0.076709000
S	0.157328000	-0.227765000	-0.185251000
C	-0.895618000	1.195683000	-0.013469000
C	2.952703000	-0.154274000	0.035315000
C	2.995145000	-1.441270000	0.602503000
C	4.134713000	0.373421000	-0.518303000
C	4.185758000	-2.169173000	0.629259000
H	2.097238000	-1.865500000	1.043570000
C	5.324728000	-0.352529000	-0.481518000
H	4.112143000	1.347471000	-0.999240000
C	5.356389000	-1.627749000	0.092013000
H	4.197797000	-3.159657000	1.076779000
H	6.225826000	0.072489000	-0.916322000
H	6.282597000	-2.195881000	0.112512000
H	2.459661000	2.630084000	0.293455000
C	-2.250603000	1.215910000	0.050731000
H	-2.688805000	2.202194000	0.200469000
C	-3.231385000	0.135393000	-0.020756000
C	-2.955954000	-1.188348000	-0.426061000
C	-4.565550000	0.440546000	0.334871000
C	-3.961583000	-2.156194000	-0.452087000
H	-1.960930000	-1.471169000	-0.750222000
C	-5.566790000	-0.526429000	0.309566000
H	-4.809368000	1.455631000	0.641288000
C	-5.270184000	-1.836820000	-0.081434000
H	-3.718103000	-3.166378000	-0.772281000
H	-6.581073000	-0.257542000	0.594463000
H	-6.048898000	-2.594607000	-0.103409000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
24	0.3546	728	84.4878	1210	2.6741
35	0.082	730	17.5141	1274	6.1675
52	0.1556	757	12.1392	1285	0.2143
59	0.6694	794	2.5056	1316	0.9549
84	0.2407	800	17.0484	1319	0.0658
107	0.4955	802	9.8843	1335	22.5771
133	0.1171	817	11.89	1427	7.2783
211	0.1351	822	0.0573	1428	16.3213
230	0.4526	880	5.3813	1475	15.9645
254	1.0196	889	6.2173	1478	17.4963
268	0.7778	897	6.9098	1540	82.8963
310	0.236	904	5.7399	1556	36.7959

340	1.2978	936	0.3794	1564	15.7155
399	0.1401	943	0.2725	1576	176.5749
401	0.134	958	0.1319	1587	7.5217
432	9.7111	964	0.1035	1589	0.9923
454	14.2235	972	1.3884	3028	7.4841
459	8.2973	975	0.1338	3051	9.2329
506	15.6854	1016	3.0213	3060	3.4686
537	2.3136	1016	4.825	3060	0.1088
570	22.3564	1068	4.1014	3066	2.3726
599	1.8265	1075	5.6963	3069	32.2427
605	2.8005	1145	0.4077	3075	15.9125
610	4.6942	1146	0.0038	3081	25.9068
640	7.976	1169	0.9987	3082	39.5396
654	6.9192	1174	2.6221	3088	17.8666
673	36.9067	1189	1.7436	3101	7.08
678	30.3163	1194	4.6791	3111	3.8571

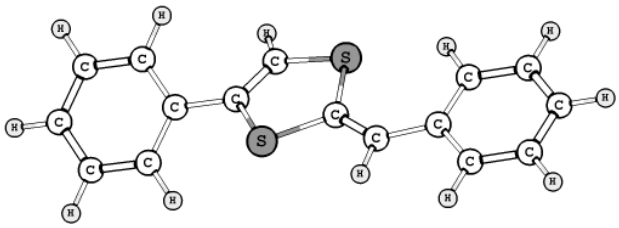
Table S6. TD DFT of 2-benzylidene-4-phenyl-1,3-dithiole (cis form) at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.



Energy = -1413.3057671 Hartree

Wavelength (nm)	*f*				
396.8	0.1256	C	1.611184000	1.973169000	0.137449000
355.8	0.0295	C	1.706055000	0.633903000	0.021190000
337.3	0.4982	S	0.031288000	2.722230000	0.076709000
319.1	0.0107	S	0.157328000	-0.227765000	-0.185251000
301.7	0.0095	C	-0.895618000	1.195683000	-0.013469000
281.5	0.0030	C	2.952703000	-0.154274000	0.035315000
267.4	0.0089	C	2.995145000	-1.441270000	0.602503000
257.5	0.0095	C	4.134713000	0.373421000	-0.518303000
252.9	0.0328	C	4.185758000	-2.169173000	0.629259000
252.7	0.1206	H	2.097238000	-1.865500000	1.043570000
		C	5.324728000	-0.352529000	-0.481518000
		H	4.112143000	1.347471000	-0.999240000
		C	5.356389000	-1.627749000	0.092013000
		H	4.197797000	-3.159657000	1.076779000
		H	6.225826000	0.072489000	-0.916322000
		H	6.282597000	-2.195881000	0.112512000
		H	2.459661000	2.630084000	0.293455000
		C	-2.250603000	1.215910000	0.050731000
		H	-2.688805000	2.202194000	0.200469000
		C	-3.231385000	0.135393000	-0.020756000
		C	-2.955954000	-1.188348000	-0.426061000
		C	-4.565550000	0.440546000	0.334871000
		C	-3.961583000	-2.156194000	-0.452087000
		H	-1.960930000	-1.471169000	-0.750222000
		C	-5.566790000	-0.526429000	0.309566000
		H	-4.809368000	1.455631000	0.641288000
		C	-5.270184000	-1.836820000	-0.081434000
		H	-3.718103000	-3.166378000	-0.772281000
		H	-6.581073000	-0.257542000	0.594463000
		H	-6.048898000	-2.594607000	-0.103409000

Table S7. Optimized structure of 2-benzylidene-4-phenyl-1,3-dithiole (*trans* form) at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)



Energy =.-1413.3054708 Hartree

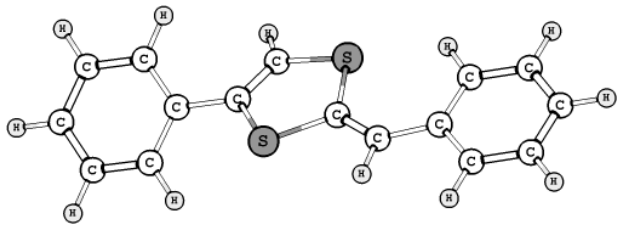
symmetry c1

C	1.771253000	1.924018000	0.730565000
C	1.792412000	0.659278000	0.265754000
S	0.234237000	2.760718000	0.865640000
S	0.208892000	-0.014688000	-0.175333000
C	-0.770952000	1.385850000	0.344345000
C	2.995894000	-0.176120000	0.085581000
C	2.960070000	-1.563794000	0.313676000
C	4.212223000	0.407302000	-0.315610000
C	4.109817000	-2.340112000	0.160550000
H	2.033273000	-2.033346000	0.632053000
C	5.361244000	-0.369820000	-0.459747000
H	4.248091000	1.470357000	-0.537195000
C	5.315703000	-1.747311000	-0.222755000
H	4.062512000	-3.409941000	0.346811000
H	6.290426000	0.099354000	-0.772979000
H	6.209874000	-2.353174000	-0.343051000
H	2.649477000	2.465221000	1.064864000
C	-2.125759000	1.322181000	0.303251000
H	-2.527976000	0.364506000	-0.025427000
C	-3.152049000	2.307952000	0.632921000
C	-2.914353000	3.658005000	0.971165000
C	-4.498423000	1.875131000	0.607345000
C	-3.969249000	4.519289000	1.277422000
H	-1.906955000	4.057082000	0.985390000
C	-5.549056000	2.735508000	0.913471000
H	-4.713406000	0.841591000	0.344056000
C	-5.291194000	4.067749000	1.254261000
H	-3.752359000	5.553800000	1.532433000
H	-6.571423000	2.366402000	0.885734000
H	-6.108003000	4.743464000	1.493689000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
16	0.2916	725	77.9211	1211	3.4209
29	0.1662	731	21.2487	1273	7.3117
40	0.1472	753	13.0719	1285	1.6883
58	0.1286	791	7.4871	1315	1.1824
86	0.0938	797	0.482	1319	0.055
112	0.2011	801	8.1961	1337	24.6437
126	0.206	816	16.2056	1427	18.3833
195	0.1322	823	0.0773	1428	6.5265
233	0.496	879	5.77	1475	22.499
258	1.4398	890	9.1143	1478	21.2039

265	0.1925	897	0.4068	1539	94.0194
316	0.0699	906	5.3325	1555	39.0485
339	1.4439	934	0.4918	1564	18.0066
399	0.07	943	0.367	1576	192.1736
400	0.1595	958	0.1011	1587	8.5847
434	13.9387	964	0.1004	1589	0.5109
454	7.1086	971	2.1375	3028	7.89
457	10.644	975	0.2922	3051	10.2715
505	19.115	1015	9.013	3060	0.6227
538	2.0876	1016	0.7857	3060	3.1986
572	25.528	1068	4.8759	3066	2.6729
600	2.2438	1076	5.9783	3069	32.8221
604	2.1748	1146	0.6273	3075	16.2566
610	2.4084	1146	0.0082	3081	24.1393
636	4.9208	1169	1.0426	3082	42.0627
659	10.7422	1176	2.5686	3088	19.0985
672	36.2644	1191	1.5459	3105	7.7548
678	31.5653	1194	4.3877	3110	4.8655

Table S8. TD DFT of 2-benzylidene-4-phenyl-1,3-dithiole (trans form) dimer at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

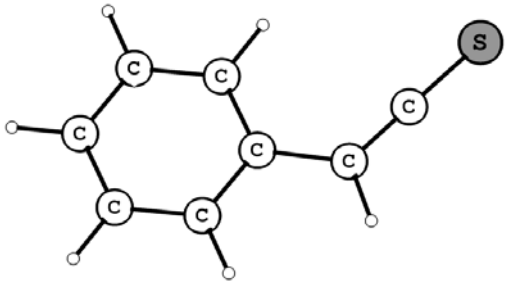


Energy = -1413.3054708 Hartree

Wavelength (nm)	*f*
396.5	0.1527
360.4	0.0038
335.8	0.5717
317.3	0.0055
300.7	0.0141
286.0	0.0014
266.0	0.0057
260.6	0.0291
255.4	0.1029
252.9	0.0044

C	1.771253000	1.924018000	0.730565000
C	1.792412000	0.659278000	0.265754000
S	0.234237000	2.760718000	0.865640000
S	0.208892000	-0.014688000	-0.175333000
C	-0.770952000	1.385850000	0.344345000
C	2.995894000	-0.176120000	0.085581000
C	2.960070000	-1.563794000	0.313676000
C	4.212223000	0.407302000	-0.315610000
C	4.109817000	-2.340112000	0.160550000
H	2.033273000	-2.033346000	0.632053000
C	5.361244000	-0.369820000	-0.459747000
H	4.248091000	1.470357000	-0.537195000
C	5.315703000	-1.747311000	-0.222755000
H	4.062512000	-3.409941000	0.346811000
H	6.290426000	0.099354000	-0.772979000
H	6.209874000	-2.353174000	-0.343051000
H	2.649477000	2.465221000	1.064864000
C	-2.125759000	1.322181000	0.303251000
H	-2.527976000	0.364506000	-0.025427000
C	-3.152049000	2.307952000	0.632921000
C	-2.914353000	3.658005000	0.971165000
C	-4.498423000	1.875131000	0.607345000
C	-3.969249000	4.519289000	1.277422000
H	-1.906955000	4.057082000	0.985390000
C	-5.549056000	2.735508000	0.913471000
H	-4.713406000	0.841591000	0.344056000
C	-5.291194000	4.067749000	1.254261000
H	-3.752359000	5.553800000	1.532433000
H	-6.571423000	2.366402000	0.885734000
H	-6.108003000	4.743464000	1.493689000

Table S9. Optimized structure of phenylthioketene at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)

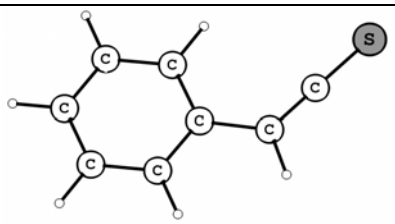


Energy = -706.6260746 Hartree

C	-3.737383000	1.237717000	-0.260640000
C	-2.867099000	0.335215000	0.347521000
C	-1.476138000	0.437588000	0.150859000
C	-0.989600000	1.470016000	-0.672210000
C	-1.864569000	2.371634000	-1.279428000
C	-3.242882000	2.261180000	-1.077426000
H	-4.807803000	1.141959000	-0.096373000
H	-3.265938000	-0.454679000	0.979022000
H	0.081749000	1.563688000	-0.835001000
H	-1.467054000	3.161767000	-1.911572000
H	-3.924610000	2.963129000	-1.550089000
C	-0.805392000	-1.507940000	1.566139000
S	-1.136240000	-2.711494000	2.509749000
C	-0.520775000	-0.491061000	0.772196000
H	0.539021000	-0.336587000	0.563561000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
54	0	782	2.1	1305	2.8
87	0.3	817	0.4	1319	3.1
210	2.7	882	27.2	1435	10.8
297	0	884	5.8	1478	23.2
377	9.1	938	0	1563	0.7
397	1.5	960	0.1	1585	54.9
400	0.2	974	0.2	1739	522.5
460	14.7	1014	2.2	3025	6.8
605	16.1	1067	6	3054	8
610	12	1145	0.2	3059	0.5
656	4.8	1160	12.2	3069	10.6
678	30.3	1170	0.5	3075	33.9
751	64.4	1244	1.2	3085	19.6

Table S10. TD DFT of phenylthioketene at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

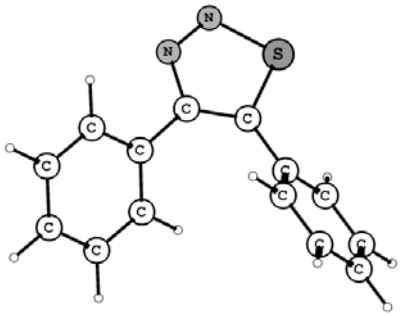


Energy = -706.6260746 Hartree

Wavelength (nm)	*f*
602.0	0
314.1	0
290.6	0
286.1	0.3385
272.7	0.1359
245.7	0.0033
227.8	0.0761
226.2	0.0077
220.1	0.0046
218.3	0.1368

C	-3.737383000	1.237717000	-0.260640000
C	-2.867099000	0.335215000	0.347521000
C	-1.476138000	0.437588000	0.150859000
C	-0.989600000	1.470016000	-0.672210000
C	-1.864569000	2.371634000	-1.279428000
C	-3.242882000	2.261180000	-1.077426000
H	-4.807803000	1.141959000	-0.096373000
H	-3.265938000	-0.454679000	0.979022000
H	0.081749000	1.563688000	-0.835001000
H	-1.467054000	3.161767000	-1.911572000
H	-3.924610000	2.963129000	-1.550089000
C	-0.805392000	-1.507940000	1.566139000
S	-1.136240000	-2.711494000	2.509749000
C	-0.520775000	-0.491061000	0.772196000
H	0.539021000	-0.336587000	0.563561000

Table S11. Optimized structure of DPT at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)



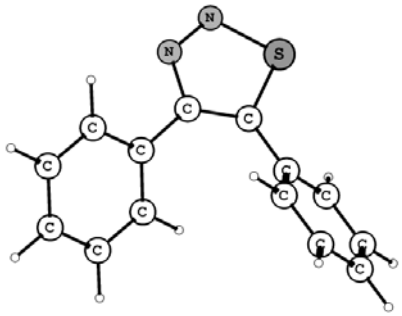
Energy = -1047.1971271 Hartree

C	-0.470844000	-0.324695000	0.295311000
C	0.861066000	-0.347142000	-0.101326000
S	-1.004077000	1.313068000	0.271308000
N	0.546205000	1.879627000	-0.267153000
N	1.356037000	0.906435000	-0.404604000
C	1.782965000	-1.499689000	-0.202576000
C	1.734625000	-2.566129000	0.710926000
C	2.760551000	-1.516733000	-1.212884000
C	2.631558000	-3.630196000	0.606270000
H	1.003810000	-2.557444000	1.513499000
C	3.655275000	-2.582594000	-1.315449000
H	2.815940000	-0.686959000	-1.910766000
C	3.592728000	-3.644869000	-0.408760000
H	2.584121000	-4.444395000	1.324939000
H	4.403540000	-2.581415000	-2.103937000
H	4.291324000	-4.473855000	-0.487931000
C	-1.387093000	-1.434327000	0.627734000
C	-1.520060000	-2.529843000	-0.243887000
C	-2.165706000	-1.399656000	1.797756000
C	-2.405410000	-3.565741000	0.053377000
H	-0.932578000	-2.561991000	-1.156566000
C	-3.048320000	-2.440223000	2.093760000
H	-2.067132000	-0.561714000	2.483145000
C	-3.170905000	-3.526372000	1.223151000
H	-2.499772000	-4.403707000	-0.632332000
H	-3.638775000	-2.400738000	3.005345000
H	-3.859682000	-4.335134000	1.452488000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
35	0.1	738	48.5	1277	3.9
42	0.1	756	17.4	1283	1.4
61	0.1	784	16.5	1301	41.9
94	1.2	826	0.7	1314	1.4
106	0.7	827	0.4	1319	4.9
134	0.9	886	30	1341	49.8
222	0.6	902	1.2	1422	8.3
254	0.5	906	4.1	1430	5.5
268	0.8	946	1.2	1453	10.4
319	0.3	948	0.4	1481	9.6
351	0.9	949	5.2	1498	2.1
397	0.1	964	0.1	1563	1.9

400	0.1	968	0.1	1566	0.9
455	5.4	976	1.1	1587	1.2
479	3.3	977	0.3	1591	3
505	7.8	1012	3.2	3059	0.3
527	22.5	1018	3	3061	1.4
561	0.8	1064	8.1	3068	2.4
606	0.2	1066	0.9	3069	10.6
609	0.1	1101	1	3076	16.1
633	4.3	1146	0	3080	31.2
665	7.3	1147	0	3085	22.6
679	21.1	1166	8.6	3091	10.7
681	47.2	1169	0.1	3091	9.6
689	19.4	1170	0.4	3094	2.8

Table S12. TD DFT of DPT at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

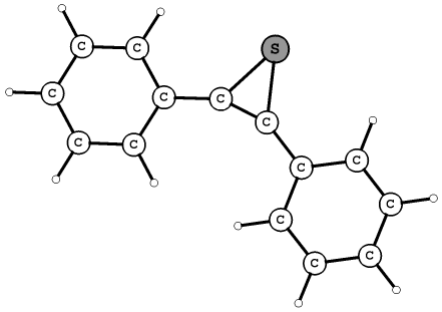


Energy = -1047.1971271 Hartree

Wavelength (nm)	*f*
322.3	0.0966
311.9	0.0464
280.4	0.0033
268.2	0.014
261.0	0.0871
257.9	0.0278
252.5	0.0429
247.3	0.015
243.5	0.0038
237.1	0.0427

C	-0.470844000	-0.324695000	0.295311000
C	0.861066000	-0.347142000	-0.101326000
S	-1.004077000	1.313068000	0.271308000
N	0.546205000	1.879627000	-0.267153000
N	1.356037000	0.906435000	-0.404604000
C	1.782965000	-1.499689000	-0.202576000
C	1.734625000	-2.566129000	0.710926000
C	2.760551000	-1.516733000	-1.212884000
C	2.631558000	-3.630196000	0.606270000
H	1.003810000	-2.557444000	1.513499000
C	3.655275000	-2.582594000	-1.315449000
H	2.815940000	-0.686959000	-1.910766000
C	3.592728000	-3.644869000	-0.408760000
H	2.584121000	-4.444395000	1.324939000
H	4.403540000	-2.581415000	-2.103937000
H	4.291324000	-4.473855000	-0.487931000
C	-1.387093000	-1.434327000	0.627734000
C	-1.520060000	-2.529843000	-0.243887000
C	-2.165706000	-1.399656000	1.797756000
C	-2.405410000	-3.565741000	0.053377000
H	-0.932578000	-2.561991000	-1.156566000
C	-3.048320000	-2.440223000	2.093760000
H	-2.067132000	-0.561714000	2.483145000
C	-3.170905000	-3.526372000	1.223151000
H	-2.499772000	-4.403707000	-0.632332000
H	-3.638775000	-2.400738000	3.005345000
H	-3.859682000	-4.335134000	1.452488000

Table S13. Optimized structure of diphenylthiirene at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)



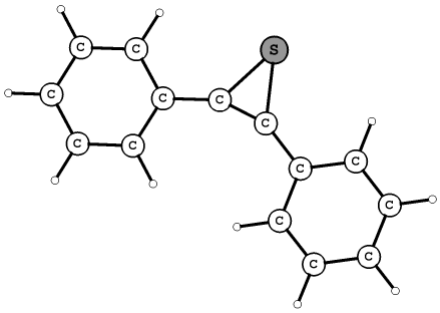
Energy = -937.6561591. Hartree

C	-0.649449000	0.670696000	-0.000118000
C	0.649618000	0.671165000	-0.000021000
S	0.000112000	2.414219000	-0.000034000
C	1.944004000	0.054916000	0.000033000
C	3.105367000	0.851642000	0.000081000
C	2.076174000	-1.351710000	0.000039000
C	4.366412000	0.256673000	0.000029000
H	3.002925000	1.932763000	0.000141000
C	3.338881000	-1.936214000	0.000013000
H	1.187200000	-1.975653000	0.000056000
C	4.488960000	-1.135837000	-0.000003000
H	5.255313000	0.881940000	0.000002000
H	3.429480000	-3.019357000	-0.000001000
H	5.472812000	-1.597318000	0.000003000
C	-1.943923000	0.054740000	-0.000076000
C	-2.076403000	-1.351880000	-0.000127000
C	-3.105163000	0.851682000	0.000025000
C	-3.339224000	-1.936127000	-0.000036000
H	-1.187566000	-1.976015000	-0.000237000
C	-4.366313000	0.256953000	0.000103000
H	-3.002491000	1.932779000	0.000055000
C	-4.489150000	-1.135531000	0.000092000
H	-3.430025000	-3.019254000	-0.000066000
H	-5.255095000	0.882390000	0.000181000
H	-5.473099000	-1.596801000	0.000206000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
33	0.5	738	0.0	1283	5.0
33	0.0	745	18.4	1288	4.6
56	0.0	815	0.0	1313	0.1
97	0.0	817	0.5	1314	2.2
133	0.0	828	7.0	1427	18.2
145	0.1	887	0.0	1427	0.0
230	3.1	890	3.9	1466	2.7
264	0.2	940	0.0	1475	40.8
279	0.1	941	0.3	1554	6.1
354	0.0	963	0.0	1555	0.1
385	0.0	963	0.0	1578	1.1
398	0.0	972	1.1	1583	22.8
402	0.0	973	0.0	1823	9.2
495	16.0	1008	1.0	3062	5.6

548	5.4	1010	7.5	3062	0.3
549	0.0	1067	5.3	3070	0.6
591	0.7	1069	4.8	3070	11.7
602	2.7	1121	0.3	3079	36.5
623	0.8	1146	0.0	3081	0.8
649	13.9	1146	0.0	3086	3.1
666	0.0	1161	0.0	3088	36.4
668	59.6	1165	0.2	3092	23.2
737	104.4	1252	8.3	3092	0.7

Table S14. TD DFT of diphenylthiirene at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.



Energy = -937.6561591 Hartree

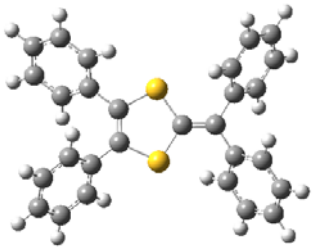
Wavelength (nm)	*f*
523.5	0.1798
345.8	0.0062
341.1	0.0000
336.0	0.0093
301.1	0.0344
285.6	0.0031
281.9	0.0089
278.5	0.6985
267.1	0.0204
266.1	0.0096

C	-0.649449000	0.670696000	-0.000118000
C	0.649618000	0.671165000	-0.000021000
S	0.000112000	2.414219000	-0.000034000
C	1.944004000	0.054916000	0.000033000
C	3.105367000	0.851642000	0.000081000
C	2.076174000	-1.351710000	0.000039000
C	4.366412000	0.256673000	0.000029000
H	3.002925000	1.932763000	0.000141000
C	3.338881000	-1.936214000	0.000013000
H	1.187200000	-1.975653000	0.000056000
C	4.488960000	-1.135837000	-0.000003000
H	5.255313000	0.881940000	0.000002000
H	3.429480000	-3.019357000	-0.000001000
H	5.472812000	-1.597318000	0.000003000
C	-1.943923000	0.054740000	-0.000076000
C	-2.076403000	-1.351880000	-0.000127000
C	-3.105163000	0.851682000	0.000025000
C	-3.339224000	-1.936127000	-0.000036000
H	-1.187566000	-1.976015000	-0.000237000
C	-4.366313000	0.256953000	0.000103000
H	-3.002491000	1.932779000	0.000055000
C	-4.489150000	-1.135531000	0.000092000
H	-3.430025000	-3.019254000	-0.000066000
H	-5.255095000	0.882390000	0.000181000
H	-5.473099000	-1.596801000	0.000206000

TD DFT B3LYP/6-311+G(d,p) using PCM model to include presence of solvent (acetonitrile):

Wavelength (nm)	*f*
482.1	0.2811
334.5	0
320.4	0.0084
313.4	0.0052
286.2	0.0455
280	0.7612
279.4	0.0142
267	0.0366
268	0.0199
265.4	0.0151

Table S15. Optimized structure of 4,5-diphenyl-2-(diphenylmethylene)-1,3-dithiole at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614).



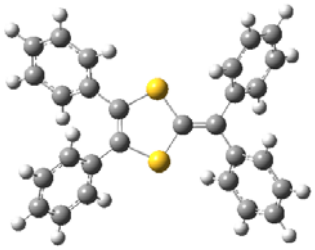
Energy = -1875.4240067 Hartree
symmetry c1

C	1.604223000	0.674339000	0.061005000
C	1.604119000	-0.674373000	-0.061102000
S	0.017378000	1.74937000	0.131479000
S	0.017344000	-.74879000	-0.131635000
C	-0.978516000	0.000044000	-0.000039000
C	2.779079000	-1.568340000	-0.200054000
C	2.890566000	-2.732592000	0.581094000
C	3.787478000	-1.288388000	-1.139054000
C	3.989419000	-3.582356000	0.440139000
H	2.118728000	-2.965402000	1.310041000
C	4.885770000	-2.137746000	-1.276239000
H	3.702865000	-0.404275000	-1.763575000
C	4.992529000	-3.287086000	-0.487024000
H	4.060968000	-4.474642000	1.056939000
H	5.655717000	-1.904808000	-2.007469000
H	5.847101000	-3.949484000	-0.598280000
C	-2.338545000	0.000020000	-0.000021000
C	-3.122838000	-1.270595000	0.025750000
C	-2.918721000	-2.247385000	1.016536000
C	-4.127705000	-1.497338000	-0.933140000
C	-3.679857000	-3.418578000	1.037491000
H	-2.168069000	-2.080666000	1.784351000
C	-4.885391000	-2.668919000	-0.915742000
H	-4.311202000	-0.746486000	-1.697377000
C	-4.663834000	-3.636541000	0.069472000
H	-3.508279000	-4.156794000	1.817278000
H	-5.650655000	-2.826103000	-1.672036000
H	-5.256209000	-4.547879000	0.085698000
C	-3.122900000	1.270585000	-0.025758000
C	-4.127904000	1.497179000	0.933033000
C	-2.918707000	2.247507000	-1.016394000
C	-4.885627000	2.668727000	0.915684000
H	-4.311470000	0.746224000	1.697153000
C	-3.679888000	3.418682000	-1.037300000
H	-2.167973000	2.080926000	-1.784157000
C	-4.663986000	3.636492000	-0.069381000
H	-5.650990000	2.825787000	1.671905000
H	-3.508227000	4.156987000	-1.816985000
H	-5.256399000	4.547805000	-0.085555000
C	2.779147000	1.568288000	0.200027000
C	3.787605000	1.288295000	1.138960000
C	2.890572000	2.732643000	-0.580998000
C	4.885848000	2.137702000	1.276211000
H	3.703068000	0.404125000	1.763408000
C	3.989376000	3.582453000	-0.439972000

H	2.118724000	2.965491000	-1.309919000
C	4.992528000	3.287141000	0.487131000
H	5.655818000	1.904725000	2.007404000
H	4.060852000	4.474806000	-1.056684000
H	5.847062000	3.949576000	0.598455000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
12	0.3744	726	76.697	1239	2.6249
20	0.4212	731	23.6753	1247	0.5814
23	0.0028	743	26.4023	1279	0.2039
36	0.1893	747	13.0101	1280	4.828
43	0.0789	791	6.2888	1280	0.5125
48	0.054	797	6.3767	1281	1.0296
49	0.0882	824	0.7631	1312	6E-4
57	0.1655	826	0.0049	1313	0.9325
62	0.0254	827	0.1628	1314	1.5301
85	0.0382	827	0.4332	1314	0.1834
89	0.0044	833	0.3147	1424	8.9913
109	0.1345	846	12.3932	1425	1.8381
119	0.3444	894	0.381	1425	6.3488
185	0.2751	898	4.3574	1427	5.6699
190	1.9375	900	0.4456	1472	11.2096
213	0.65	901	3E-4	1473	7.6134
222	0.6367	944	2.0982	1476	16.5128
231	0.0674	946	0.4609	1477	17.6381
258	0.3596	946	0.3895	1524	150.9362
280	0.2324	947	0.1229	1557	18.5271
284	0.3743	947	0.3987	1560	2.9778
326	0.1033	960	0.02	1562	3.225
344	0.5872	962	0.069	1562	8.4035
380	1.0948	964	0.3401	1578	70.0792
399	0.0321	965	0.3155	1583	11.9033
399	0.3646	969	0.0033	1586	18.2407
400	0.2052	975	2.2931	1586	10.6415
401	0.014	976	0.4318	1587	0.0363
426	0.7193	976	0.1179	3054	3.8159
443	32.2105	976	0.2584	3054	2.8395
467	5.1095	1013	5.0855	3058	1.5673
482	2.9619	1014	3.7675	3058	2.0452
497	0.7396	1017	1.9382	3061	1.4607
507	4.3767	1018	12.6202	3061	7.9069
594	0.5926	1065	0.5508	3066	9.8573
595	7.0012	1066	9.9237	3066	0.0688
599	4.096	1066	0.2298	3071	34.3865
603	9.7682	1069	8.4134	3071	8.293
607	1.1062	1144	0.0413	3075	33.962
610	1.6833	1144	0.0526	3075	11.5491
617	0.7687	1145	0.0462	3077	20.5522
626	5.4947	1145	0.0136	3077	35.7289
632	47.1985	1146	0.0057	3083	30.8209
634	2.9704	1165	0.0354	3083	36.9523
681	33.3504	1165	3.5722	3083	22.8212
682	24.1714	1166	0.0165	3083	2.2457
682	47.154	1167	0.8039	3090	11.6225
685	52.0837	1169	0.115	3090	5.8386

Table S16. TD DFT of 4,5-diphenyl-2-(diphenylmethylene)-1,3-dithiole at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

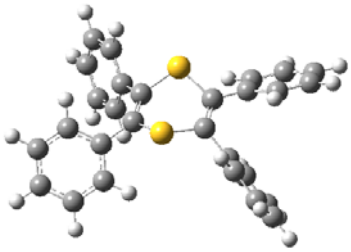


Energy = -1875.4240067 Hartree

Wavelength (nm)	*f*
433.3	0.0467
376	4E-4
362.5	0.2751
339.2	0.0113
335.7	0.095
334.4	0.0511
318.2	0.0018
307.3	0.0053
298.9	0.0206
283.9	0.0024

C	1.604223000	0.674339000	0.061005000
C	1.604119000	-0.674373000	-0.061102000
S	0.017378000	1.74937000	0.131479000
S	0.017344000	-.74879000	-0.131635000
C	-0.978516000	0.000044000	-0.000039000
C	2.779079000	-1.568340000	-0.200054000
C	2.890566000	-2.732592000	0.581094000
C	3.787478000	-1.288388000	-1.139054000
C	3.989419000	-3.582356000	0.440139000
H	2.118728000	-2.965402000	1.310041000
C	4.885770000	-2.137746000	-1.276239000
H	3.702865000	-0.404275000	-1.763575000
C	4.992529000	-3.287086000	-0.487024000
H	4.060968000	-4.474642000	1.056939000
H	5.655717000	-1.904808000	-2.007469000
H	5.847101000	-3.949484000	-0.598280000
C	-2.338545000	0.000020000	-0.000021000
C	-3.122838000	-1.270595000	0.025750000
C	-2.918721000	-2.247385000	1.016536000
C	-4.127705000	-1.497338000	-0.933140000
C	-3.679857000	-3.418578000	1.037491000
H	-2.168069000	-2.080666000	1.784351000
C	-4.885391000	-2.668919000	-0.915742000
H	-4.311202000	-0.746486000	-1.697377000
C	-4.663834000	-3.636541000	0.069472000
H	-3.508279000	-4.156794000	1.817278000
H	-5.650655000	-2.826103000	-1.672036000
H	-5.256209000	-4.547879000	0.085698000
C	-3.122900000	1.270585000	-0.025758000
C	-4.127904000	1.497179000	0.933033000
C	-2.918707000	2.247507000	-1.016394000
C	-4.885627000	2.668727000	0.915684000
H	-4.311470000	0.746224000	1.697153000
C	-3.679888000	3.418682000	-1.037300000
H	-2.167973000	2.080926000	-1.784157000
C	-4.663986000	3.636492000	-0.069381000
H	-5.650990000	2.825787000	1.671905000
H	-3.508227000	4.156987000	-1.816985000
H	-5.256399000	4.547805000	-0.085555000
C	2.779147000	1.568288000	0.200027000
C	3.787605000	1.288295000	1.138960000
C	2.890572000	2.732643000	-0.580998000
C	4.885848000	2.137702000	1.276211000
H	3.703068000	0.404125000	1.763408000
C	3.989376000	3.582453000	-0.439972000
H	2.118724000	2.965491000	-1.309919000
C	4.992528000	3.287141000	0.487131000
H	5.655818000	1.904725000	2.007404000
H	4.060852000	4.474806000	-1.056684000
H	5.847062000	3.949576000	0.598455000

Table S17. Optimized structure of tetraphenyl-1,4-dithiine at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614).



Energy = -1875.4156576 Hartree

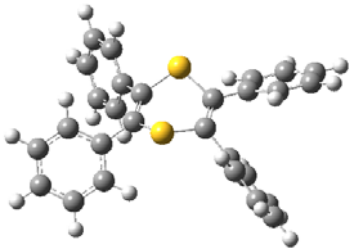
symmetry c1

C	-1.420078000	0.666025000	-0.704407000
C	-1.387116000	-0.686254000	-0.660809000
C	1.420089000	-0.666295000	-0.704223000
C	1.386910000	0.686005000	-0.660968000
S	0.019847000	-1.572930000	-1.356785000
S	-0.019862000	1.572021000	-1.357937000
C	2.563080000	-1.518166000	-0.278769000
C	3.861074000	-1.241537000	-0.744765000
C	2.372615000	-2.632375000	0.558022000
C	4.939540000	-2.042016000	-0.366585000
H	4.019542000	-0.398266000	-1.410095000
C	3.453870000	-3.426884000	0.941816000
H	1.372836000	-2.871070000	0.908705000
C	4.741602000	-3.134957000	0.482177000
H	5.934375000	-1.814124000	-0.740941000
H	3.288473000	-4.278145000	1.597484000
H	5.581842000	-3.758993000	0.775868000
C	-2.562811000	1.518183000	-0.278835000
C	-3.861082000	1.241617000	-0.744118000
C	-2.371743000	2.632739000	0.557345000
C	-4.939206000	2.042468000	-0.365775000
H	-4.020028000	0.398133000	-1.409057000
C	-3.452667000	3.427627000	0.941318000
H	-1.371751000	2.871446000	0.907411000
C	-4.740667000	3.135744000	0.482428000
H	-5.934261000	1.814639000	-0.739585000
H	-3.286770000	4.279139000	1.596535000
H	-5.580667000	3.760050000	0.776230000
C	2.407734000	1.560469000	-0.021631000
C	2.820752000	1.341687000	1.303751000
C	2.953308000	2.649909000	-0.723189000
C	3.761492000	2.180087000	1.904326000
H	2.399955000	0.511470000	1.863285000
C	3.896228000	3.485975000	-0.122949000
H	2.643448000	2.839264000	-1.748192000
C	4.305100000	3.253945000	1.193646000
H	4.066947000	1.994545000	2.931102000
H	4.311043000	4.318853000	-0.685164000
H	5.037551000	3.906137000	1.662329000
C	-2.408151000	-1.560570000	-0.021587000
C	-2.954212000	-2.649537000	-0.723460000
C	-2.820843000	-1.342122000	1.303957000
C	-3.897284000	-3.485545000	-0.123335000
H	-2.644652000	-2.838591000	-1.748611000
C	-3.761737000	-2.180431000	1.904387000

H	-2.399671000	-0.512220000	1.863682000
C	-4.305818000	-3.253875000	1.193413000
H	-4.312472000	-4.318070000	-0.685797000
H	-4.066978000	-1.995164000	2.931276000
H	-5.038396000	-3.905984000	1.662011000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
23	1E-4	722	43.1125	1216	0.111
27	0.2619	724	68.2698	1227	0.7064
35	0.0156	747	6.7133	1278	0.0014
39	0.1014	748	21.9995	1278	0.5658
40	9E-4	777	10.4635	1281	0.1595
48	0.0734	803	8.4422	1281	1.2188
48	0.1398	813	30.7166	1313	0.6827
57	0.0607	823	0.1509	1313	1.8463
60	0.0384	823	0.4213	1314	0.7147
92	0.8462	826	0.0024	1314	0.8692
111	0.1857	826	0.7082	1425	1.7359
117	0.1761	834	1.7448	1425	0.7919
168	0.4722	891	0.8861	1426	7.0214
184	0.0434	893	3.1439	1426	7.1147
192	0.7684	900	0.282	1470	10.6306
209	0.0025	901	1.1443	1472	1.9478
212	3.5313	933	3.7265	1475	0.5442
225	1.3254	943	0.0498	1475	16.3173
258	0.9377	944	0.0156	1540	41.7682
259	0.0136	948	0.3559	1556	0.0044
317	0.219	948	0.1821	1561	3.6446
323	0.0308	950	2.6589	1562	2.1865
346	0.1683	962	0.0781	1564	6.4573
361	0.5692	962	0.659	1575	0.017
397	0.0743	965	0.2686	1584	8.5673
398	0.0032	965	0.0431	1584	0.0016
402	0.0158	975	1.6197	1585	0.1741
402	0.0485	976	0.0502	1585	13.9153
415	0.0296	976	1.508	3056	5.6214
466	5.1829	976	0.027	3056	0.908
484	0.3251	1014	6.9868	3058	1.0852
493	13.0999	1014	0.7123	3058	0.0078
507	6.6094	1016	2E-4	3062	3.4442
525	1.4489	1017	11.1457	3062	1.2103
577	3.4098	1066	0.2342	3067	11.8743
590	3.8549	1066	1.4765	3067	6.8807
599	0.0854	1068	11.7092	3071	7.9714
606	4.0812	1069	6.8761	3071	33.387
609	1.0013	1145	0.0124	3078	59.252
610	0.0269	1145	0.0442	3078	2.2197
614	1.5593	1145	0.2795	3081	58.0656
619	36.0042	1145	0.0024	3081	2.753
625	0.0085	1150	14.7478	3086	8.658
646	1.7876	1161	0.9534	3086	18.7016
680	58.7604	1167	2.4004	3087	8.9342
680	27.9889	1167	0.0936	3088	12.4579
681	22.8348	1168	0.6705	3090	14.2551
681	25.5033	1169	0.9127	3090	0.9811

Table S18. TD DFT of tetraphenyl-1,4-dithiine at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

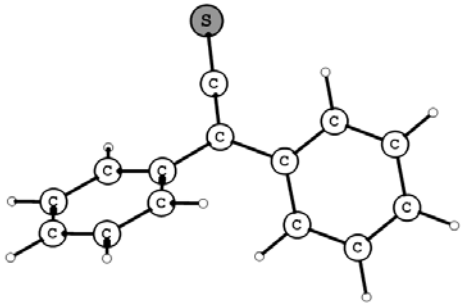


Energy = -1875.4156576 Hartree

Wavelength (nm)	*f*
398.5	0.0000
344.7	0.1697
307.1	0.3132
296.8	0.0001
295.3	0.0126
293.9	0.0047
283.5	0.0010
282.3	0.0032
274.7	0.0022
274.6	0.0289
274.2	0.1765

C	-1.420078000	0.666025000	-0.704407000
C	-1.387116000	-0.686254000	-0.660809000
C	1.420089000	-0.666295000	-0.704223000
C	1.386910000	0.686005000	-0.660968000
S	0.019847000	-1.572930000	-1.356785000
S	-0.019862000	1.572021000	-1.357937000
C	2.563080000	-1.518166000	-0.278769000
C	3.861074000	-1.241537000	-0.744765000
C	2.372615000	-2.632375000	0.558022000
C	4.939540000	-2.042016000	-0.366585000
H	4.019542000	-0.398266000	-1.410095000
C	3.453870000	-3.426884000	0.941816000
H	1.372836000	-2.871070000	0.908705000
C	4.741602000	-3.134957000	0.482177000
H	5.934375000	-1.814124000	-0.740941000
H	3.288473000	-4.278145000	1.597484000
H	5.581842000	-3.758993000	0.775868000
C	-2.562811000	1.518183000	-0.278835000
C	-3.861082000	1.241617000	-0.744118000
C	-2.371743000	2.632739000	0.557345000
C	-4.939206000	2.042468000	-0.365775000
H	-4.020028000	0.398133000	-1.409057000
C	-3.452667000	3.427627000	0.941318000
H	-1.371751000	2.871446000	0.907411000
C	-4.740667000	3.135744000	0.482428000
H	-5.934261000	1.814639000	-0.739585000
H	-3.286770000	4.279139000	1.596535000
H	-5.580667000	3.760050000	0.776230000
C	2.407734000	1.560469000	-0.021631000
C	2.820752000	1.341687000	1.303751000
C	2.953308000	2.649909000	-0.723189000
C	3.761492000	2.180087000	1.904326000
H	2.399955000	0.511470000	1.863285000
C	3.896228000	3.485975000	-0.122949000
H	2.643448000	2.839264000	-1.748192000
C	4.305100000	3.253945000	1.193646000
H	4.066947000	1.994545000	2.931102000
H	4.311043000	4.318853000	-0.685164000
H	5.037551000	3.906137000	1.662329000
C	-2.408151000	-1.560570000	-0.021587000
C	-2.954212000	-2.649537000	-0.723460000
C	-2.820843000	-1.342122000	1.303957000
C	-3.897284000	-3.485545000	-0.123335000
H	-2.644652000	-2.838591000	-1.748611000
C	-3.761737000	-2.180431000	1.904387000
H	-2.399671000	-0.512220000	1.863682000
C	-4.305818000	-3.253875000	1.193413000
H	-4.312472000	-4.318070000	-0.685797000
H	-4.066978000	-1.995164000	2.931276000
H	-5.038396000	-3.905984000	1.662011000

Table S19. Optimized structure of diphenylthioketene at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)



Energy = -937.6863672Hartree

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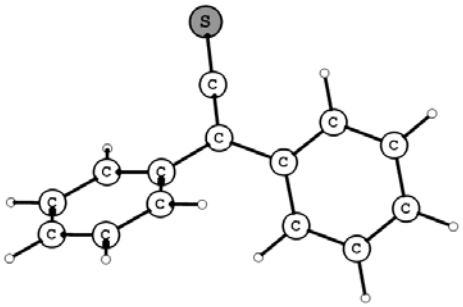
C	-1.406242000	0.440311000	-0.008092000
C	-1.106362000	1.417648000	-0.974556000
C	-2.028074000	2.419416000	-1.280958000
C	-3.267619000	2.462442000	-0.634625000
H	-4.532615000	1.522263000	0.840858000
H	-2.892250000	-0.240390000	1.402797000
H	-0.151003000	1.385942000	-1.490274000
H	-1.778462000	3.164978000	-2.031882000
H	-3.984035000	3.243524000	-0.875257000
C	-0.879474000	-1.870899000	0.529123000
S	-1.412920000	-3.316251000	0.809033000
C	-0.427819000	-0.645651000	0.293295000
C	1.042015000	-0.392734000	0.337252000
C	1.538953000	0.811894000	0.867427000
C	1.959670000	-1.355778000	-0.118402000
C	2.913244000	1.042803000	0.938154000
H	0.845135000	1.564451000	1.230499000
C	3.333979000	-1.124557000	-0.039757000
H	1.591622000	-2.283614000	-0.548503000
C	3.817708000	0.076117000	0.487298000
H	3.277969000	1.979342000	1.352834000
H	4.026602000	-1.880892000	-0.400495000
H	4.887669000	0.258455000	0.543684000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
20	0.4	748	50.5	1277	0.1
53	0.4	822	0.1	1289	2.8
71	0.3	825	0	1315	0.9
73	0.1	880	1	1315	2.8
90	0.3	891	4.6	1425	2.9
208	0.5	900	3.2	1430	17.1
218	0.5	944	0.5	1474	9.2
279	0	945	17.4	1475	35.6
322	2.4	947	27.9	1560	2
351	0.4	963	0.2	1562	0.1
398	0.7	964	1.3	1581	22.7
402	0	975	0.2	1583	38.4
436	2.8	975	1.5	**1719**	**454.2**
459	4.1	1015	0.1	3057	2.7

493	2.5	1015	8.8	3058	1.9
582	10.6	1067	5.6	3064	5.1
607	0.1	1069	0.3	3065	4.3
612	3.4	1145	0.1	3074	16.4
624	13.4	1145	0	3074	19.5
670	16.4	1166	0.1	3081	48.6
680	56.2	1167	0.2	3082	3.2
682	18.6	1171	0.5	3087	12.1
736	27.9	1235	6	3087	12.8

Table S20. TD DFT of diphenylthioketene at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

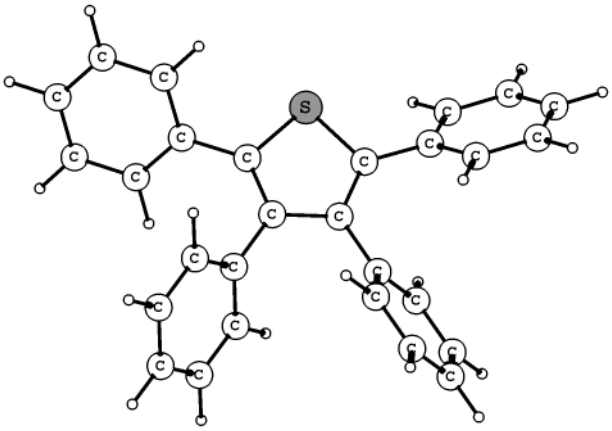


Energy = -937.6863672 Hartree

Wavelength (nm)	*f*
616.3	0.0036
313.6	0.0104
310.6	0.0109
301.6	0.0006
299.5	0.1391
295.1	0.008
286.8	0.2096
285.4	0.0892
268.8	0.0229
250.8	0.0064

C	-3.575564000	1.495021000	0.325863000
C	-2.652848000	0.495675000	0.639780000
C	-1.406242000	0.440311000	-0.008092000
C	-1.106362000	1.417648000	-0.974556000
C	-2.028074000	2.419416000	-1.280958000
C	-3.267619000	2.462442000	-0.634625000
H	-4.532615000	1.522263000	0.840858000
H	-2.892250000	-0.240390000	1.402797000
H	-0.151003000	1.385942000	-1.490274000
H	-1.778462000	3.164978000	-2.031882000
H	-3.984035000	3.243524000	-0.875257000
C	-0.879474000	-1.870899000	0.529123000
S	-1.412920000	-3.316251000	0.809033000
C	-0.427819000	-0.645651000	0.293295000
C	1.042015000	-0.392734000	0.337252000
C	1.538953000	0.811894000	0.867427000
C	1.959670000	-1.355778000	-0.118402000
C	2.913244000	1.042803000	0.938154000
H	0.845135000	1.564451000	1.230499000
C	3.333979000	-1.124557000	-0.039757000
H	1.591622000	-2.283614000	-0.548503000
C	3.817708000	0.076117000	0.487298000
H	3.277969000	1.979342000	1.352834000
H	4.026602000	-1.880892000	-0.400495000
H	4.887669000	0.258455000	0.543684000

Table S21. Optimized structure of tetraphenylthiophene at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)



Energy = -1477.2621483 Hartree

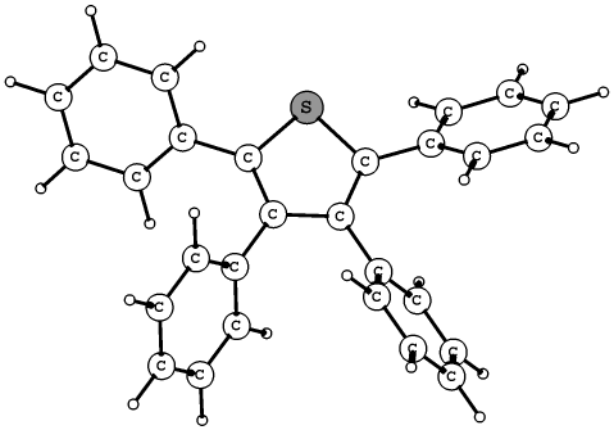
symmetry c1

C	1.262299000	-1.117365000	0.009159000
C	0.724165000	0.158230000	0.006983000
C	-0.724258000	0.158304000	-0.007451000
C	-1.262589000	-1.117190000	-0.009641000
S	-0.000123000	-2.322547000	-0.000285000
C	-2.671662000	-1.559877000	0.034599000
C	-3.116108000	-2.617551000	-0.780961000
C	-3.593991000	-0.962264000	0.913643000
C	-4.438943000	-3.060028000	-0.723214000
H	-2.422609000	-3.085165000	-1.475417000
C	-4.916901000	-1.401955000	0.965449000
H	-3.267383000	-0.156116000	1.562784000
C	-5.346436000	-2.452432000	0.148434000
H	-4.760466000	-3.876320000	-1.365294000
H	-5.612215000	-0.926631000	1.652914000
H	-6.377204000	-2.794642000	0.192507000
C	-1.549388000	1.398052000	-0.030062000
C	-1.434689000	2.361491000	0.986253000
C	-2.463908000	1.629642000	-1.071021000
C	-2.216551000	3.518250000	0.966051000
H	-0.729518000	2.201457000	1.797362000
C	-3.245223000	2.786923000	-1.093278000
H	-2.560881000	0.895403000	-1.866462000
C	-3.125679000	3.735466000	-0.073504000
H	-2.114015000	4.250432000	1.763301000
H	-3.946671000	2.946880000	-1.908523000
H	-3.733424000	4.636702000	-0.089888000
C	1.549460000	1.397854000	0.029921000
C	1.435126000	2.361412000	-0.986337000
C	2.463945000	1.629102000	1.070974000
C	2.217218000	3.518001000	-0.965904000
H	0.730034000	2.201599000	-1.797559000
C	3.245513000	2.786215000	1.093451000
H	2.560711000	0.894730000	1.866324000
C	3.126256000	3.734918000	0.073802000
H	2.114939000	4.250296000	-1.763084000
H	3.946924000	2.945905000	1.908780000
H	3.734192000	4.636022000	0.090355000
C	2.671408000	-1.560063000	-0.034759000
C	3.115709000	-2.617542000	0.781123000
C	3.593858000	-0.962638000	-0.913791000
C	4.438563000	-3.060016000	0.723707000
H	2.422089000	-3.085001000	1.475561000
C	4.916781000	-1.402329000	-0.965273000

H	3.267340000	-0.156649000	-1.563170000
C	5.346185000	-2.452612000	-0.147935000
H	4.759992000	-3.876142000	1.366044000
H	5.612213000	-0.927178000	-1.652736000
H	6.376968000	-2.794809000	-0.191763000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
28	0.0093	746	33.3437	1273	1.7622
40	0.1124	757	2.2764	1277	0.7077
40	0.1532	775	24.4495	1280	0.5834
44	0.5332	798	0.0526	1285	0.474
51	0.1539	824	0.2092	1310	0.0093
52	0.3181	824	0.227	1311	1.2971
55	0.0484	826	0.0519	1314	0.0231
61	0.0755	827	0.0023	1314	1.1059
65	0.0082	855	2.4485	1336	1.7813
111	0.7283	895	3.2424	1416	0.0016
121	0.1473	897	1.8939	**1423**	**5.3299**
132	0.2102	898	0.8764	**1427**	**7.5789**
212	0.4101	901	6.4848	1429	1.9635
216	0.0013	926	1.571	1438	4.003
220	0.1867	945	0.1929	**1468**	**25.5706**
223	0.0051	945	0.3422	**1479**	**18.2888**
232	0.0049	946	0.0603	1480	1.7442
257	0.2613	946	0.0096	1490	3.297
265	0.0146	961	0.3809	**1517**	**8.9404**
340	0.1349	962	0.1953	1561	4.4427
341	1.3648	963	0.263	1561	0.5909
385	0.7339	963	0.1029	1563	0.1055
400	0.0322	966	2.7749	1565	0.8508
400	0.23	975	0.0194	**1586**	**29.8953**
401	0.0282	975	0.921	**1587**	**7.7909**
401	0.1328	977	0.0885	1589	0.7723
430	0.0098	977	1.107	1589	7.764
478	3.883	1012	5.9362	3054	0.7837
493	6.3431	**1014**	**11.2662**	3054	1.6085
497	0.0703	1017	3.7792	3056	4.669
515	5.2103	1020	1.4779	3056	0.9945
578	19.0525	1061	2.3741	3062	7.3505
595	0.1961	1064	4.2147	3062	0.3981
601	11.7445	1064	0.7712	3064	4.1694
607	0.4777	**1068**	**12.2626**	3064	5.3512
609	0.2577	1098	0.2281	3071	32.179
610	0.6851	1144	0.0447	3072	13.9946
618	0.2868	1144	0.0046	3073	42.8362
634	0.2688	1145	0.0612	3073	3.1873
648	2.0781	1145	0.0028	3078	3.3884
680	29.9342	1160	2.1994	3078	50.6476
681	39.6524	1165	0.0239	3082	38.3398
683	53.4246	1166	0.2028	3082	27.2103
684	15.4022	1169	0.351	3084	18.686
703	0.1258	1169	1.6488	3084	8.0426
703	46.7927	1197	5.7612	3093	10.956
733	54.343	1271	2.6429	3093	2.365

Table S22. TD DFT of tetraphenylthiophene at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

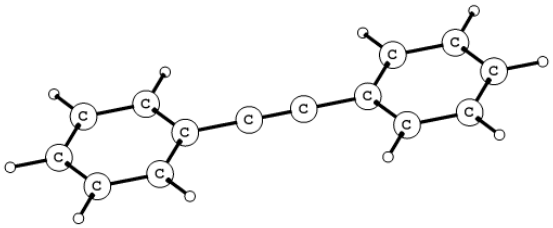


Energy = -1477.2621483 Hartree

Wavelength (nm)	*f*
327.7	0.3014
295.3	0.0211
284.3	0.2515
281.3	0.0764
280.1	0.0255
270.0	0
264.4	0.0414
261.3	0.0013
259.5	0.0118
255.9	0.0724
255.8	0.0093

C	1.262299000	-1.117365000	0.009159000
C	0.724165000	0.158230000	0.006983000
C	-0.724258000	0.158304000	-0.007451000
C	-1.262589000	-1.117190000	-0.009641000
S	-0.000123000	-2.322547000	-0.000285000
C	-2.671662000	-1.559877000	0.034599000
C	-3.116108000	-2.617551000	-0.780961000
C	-3.593991000	-0.962264000	0.913643000
C	-4.438943000	-3.060028000	-0.723214000
H	-2.422609000	-3.085165000	-1.475417000
C	-4.916901000	-1.401955000	0.965449000
H	-3.267383000	-0.156116000	1.562784000
C	-5.346436000	-2.452432000	0.148434000
H	-4.760466000	-3.876320000	-1.365294000
H	-5.612215000	-0.926631000	1.652914000
H	-6.377204000	-2.794642000	0.192507000
C	-1.549388000	1.398052000	-0.030062000
C	-1.434689000	2.361491000	0.986253000
C	-2.463908000	1.629642000	-1.071021000
C	-2.216551000	3.518250000	0.966051000
H	-0.729518000	2.201457000	1.797362000
C	-3.245223000	2.786923000	-1.093278000
H	-2.560881000	0.895403000	-1.866462000
C	-3.125679000	3.735466000	-0.073504000
H	-2.114015000	4.250432000	1.763301000
H	-3.946671000	2.946880000	-1.908523000
H	-3.733424000	4.636702000	-0.089888000
C	1.549460000	1.397854000	0.029921000
C	1.435126000	2.361412000	-0.986337000
C	2.463945000	1.629102000	1.070974000
C	2.217218000	3.518001000	-0.965904000
H	0.730034000	2.201599000	-1.797559000
C	3.245513000	2.786215000	1.093451000
H	2.560711000	0.894730000	1.866324000
C	3.126256000	3.734918000	0.073802000
H	2.114939000	4.250296000	-1.763084000
H	3.946924000	2.945905000	1.908780000
H	3.734192000	4.636022000	0.090355000
C	2.671408000	-1.560063000	-0.034759000
C	3.115709000	-2.617542000	0.781123000
C	3.593858000	-0.962638000	-0.913791000
C	4.438563000	-3.060016000	0.723707000
H	2.422089000	-3.085001000	1.475561000
C	4.916781000	-1.402329000	-0.965273000
H	3.267340000	-0.156649000	-1.563170000
C	5.346185000	-2.452612000	-0.147935000
H	4.759992000	-3.876142000	1.366044000
H	5.612213000	-0.927178000	-1.652736000
H	6.376968000	-2.794809000	-0.191763000

Table S23. Optimized structure of diphenylacetylene at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)



Energy = -539.4828082 Hartree

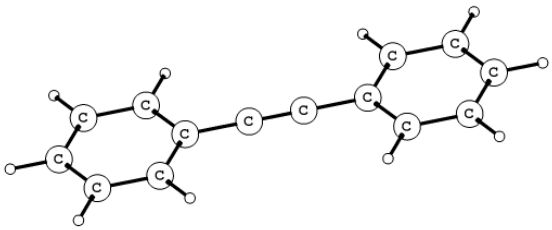
symmetry c1

C	-0.608935000	-0.000055000	-0.000026000
C	0.608943000	-0.000081000	-0.000182000
C	-2.035426000	-0.000035000	-0.000014000
C	-2.753584000	-1.214270000	0.000173000
C	-2.753511000	1.214247000	-0.000163000
C	-4.147502000	-1.209582000	0.000202000
H	-2.206828000	-2.152739000	0.000300000
C	-4.147429000	1.209640000	-0.000129000
H	-2.206697000	2.152682000	-0.000301000
C	-4.850081000	0.000047000	0.000047000
H	-4.687583000	-2.152971000	0.000346000
H	-4.687454000	2.153060000	-0.000245000
H	-5.936947000	0.000074000	0.000074000
C	2.035426000	-0.000052000	-0.000098000
C	2.753595000	-1.214277000	-0.000211000
C	2.753496000	1.214240000	0.000125000
C	4.147514000	-1.209573000	-0.000111000
H	2.206852000	-2.152753000	-0.000375000
C	4.147414000	1.209648000	0.000220000
H	2.206669000	2.152667000	0.000225000
C	4.850080000	0.000063000	0.000101000
H	4.687606000	-2.152955000	-0.000202000
H	4.687429000	2.153074000	0.000390000
H	5.936946000	0.000102000	0.000181000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
23	0	819	0	1293	6.1894
46	0.5692	820	0	1311	0
51	1.3067	824	1.2297	1311	0.7205
139	0	892	0	1424	0
142	0	894	5.7307	1426	7.1206
250	0	941	0	1468	0
284	0.2776	941	0	1485	43.818
394	0	963	0	1554	0
395	0	963	0.0723	1555	2.8585
397	0	974	0	1582	0
455	1.5929	974	0.0017	1590	31.6176
515	17.41	1010	0	2214	0
524	0	1012	9.329	3059	4.5283
525	16.1249	1062	0	3059	1E-4
539	0	1064	11.1672	3067	2E-4
610	8E-4	1118	0	3067	12.9323

612	0	1145	0	3078	45.6457
672	0	1145	0.0093	3078	0
673	68.0407	1163	0.1162	3085	1E-4
687	0	1164	0	3085	49.5638
737	0	1273	0	3089	22.9319
741	100.9781	1277	0.0691	3089	0

Table S24. TD DFT of diphenylacetylene at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

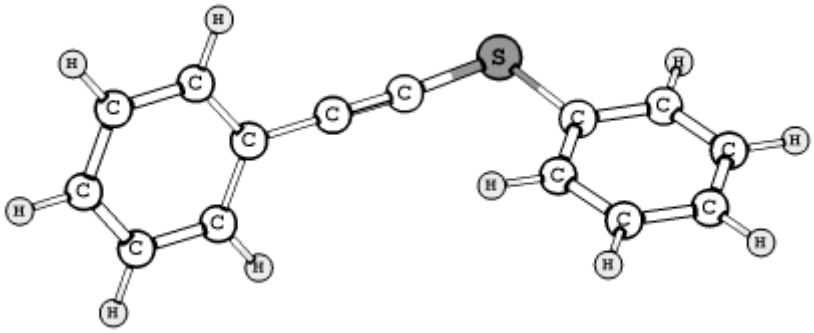


Energy = -539.4828082 Hartree

Wavelength (nm)	*f*
305.4	0.9435
270.4	0.0011
268.5	0
262.5	0
239.6	0
235.5	0.131
234.8	0
231.5	0.0018
220.4	0
217.9	0
213.5	0

C	-0.608935000	-0.000055000	-0.000026000
C	0.608943000	-0.000081000	-0.000182000
C	-2.035426000	-0.000035000	-0.000014000
C	-2.753584000	-1.214270000	0.000173000
C	-2.753511000	1.214247000	-0.000163000
C	-4.147502000	-1.209582000	0.000202000
H	-2.206828000	-2.152739000	0.000300000
C	-4.147429000	1.209640000	-0.000129000
H	-2.206697000	2.152682000	-0.000301000
C	-4.850081000	0.000047000	0.000047000
H	-4.687583000	-2.152971000	0.000346000
H	-4.687454000	2.153060000	-0.000245000
H	-5.936947000	0.000074000	0.000074000
C	2.035426000	-0.000052000	-0.000098000
C	2.753595000	-1.214277000	-0.000211000
C	2.753496000	1.214240000	0.000125000
C	4.147514000	-1.209573000	-0.000111000
H	2.206852000	-2.152753000	-0.000375000
C	4.147414000	1.209648000	0.000220000
H	2.206669000	2.152667000	0.000225000
C	4.850080000	0.000063000	0.000101000
H	4.687606000	-2.152955000	-0.000202000
H	4.687429000	2.153074000	0.000390000
H	5.936946000	0.000102000	0.000181000

Table S25. Optimized structure of phenyl(2-phenylethynyl)sulfane at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)



Energy = -937.6585615 Hartree

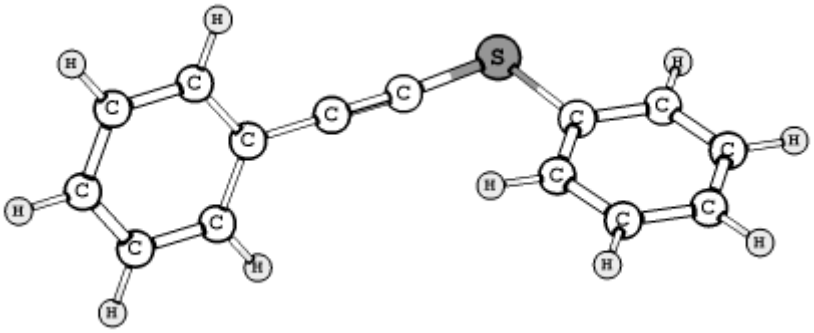
symmetry c1

C	1.226863000	-0.684998000	-0.107057000
C	0.074686000	-1.083277000	-0.153059000
S	-1.456971000	-1.783077000	-0.244466000
C	2.570587000	-0.203246000	-0.049418000
C	3.076408000	0.633407000	-1.065934000
C	3.413745000	-0.558805000	1.023812000
C	4.386840000	1.105106000	-1.003430000
H	2.432003000	0.904835000	-1.896979000
C	4.726094000	-0.091123000	1.073832000
H	3.027735000	-1.201831000	1.809298000
C	5.215849000	0.743317000	0.063591000
H	4.763984000	1.751782000	-1.791477000
H	5.367042000	-0.374734000	1.904604000
H	6.238416000	1.109160000	0.107234000
C	-2.586774000	-0.393041000	-0.037853000
C	-2.170716000	0.907516000	0.260183000
C	-3.950676000	-0.683809000	-0.181178000
C	-3.126191000	1.916548000	0.413058000
H	-1.113916000	1.129245000	0.371376000
C	-4.894962000	0.331669000	-0.023387000
H	-4.274219000	-1.695128000	-0.416767000
C	-4.487660000	1.636217000	0.273713000
H	-2.798228000	2.926967000	0.644424000
H	-5.951180000	0.100573000	-0.135989000
H	-5.224653000	2.425470000	0.394493000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
11	0.3793	718	68.7749	1274	0.338
17	0.089	745	40.4609	1283	1.5945
30	0.3669	814	0.0178	1310	0.5486
73	0.5155	824	0.1989	1310	0.8467
112	0.6813	846	0.1993	1425	4.65
171	1.0563	875	1.0882	1426	7.8935
227	0.4434	901	2.1669	1463	**42.3125**
254	2.5508	939	0.0132	1474	**15.2505**
278	1.2846	945	0.0199	1556	1.106
364	1.9452	960	0.0858	1566	2.2114
387	0.7586	966	0.0213	1573	**56.7743**
397	0.0934	973	2.9482	1585	3.0758

398	0.0652	975	0.5111	2165	0.1041
449	4.4244	1006	24.3474	3057	2.3661
460	9.5155	1012	5.0699	3061	1.0838
479	0.6011	1052	17.8618	3064	0.3991
542	15.6629	1063	5.2124	3069	6.7091
604	0.5307	1066	2.4226	3073	23.4363
610	0.0139	1145	0.239	3079	23.5717
638	2.8477	1146	0.0586	3085	25.2428
669	13.3689	1162	1.0214	3087	20.5648
671	14.0264	1166	2.3941	3091	8.9238
676	40.5191	1216	1.31	3092	7.1424

Table S26. TD DFT of phenyl(2-phenylethynyl)sulfane at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.



Energy = -937.6585615 Hartree

Wavelength (nm)	*f*
352.5	0.0536
274.8	0.0076
271.1	0.0014
262.7	0.1101
258.3	0.6664
250.3	0.0067
243.0	0.001
238.8	0.0207
236.5	0.017
234.6	0.0212
228.5	0.0082

C	1.226863000	-0.684998000	-0.107057000
C	0.074686000	-1.083277000	-0.153059000
S	-1.456971000	-1.783077000	-0.244466000
C	2.570587000	-0.203246000	-0.049418000
C	3.076408000	0.633407000	-1.065934000
C	3.413745000	-0.558805000	1.023812000
C	4.386840000	1.105106000	-1.003430000
H	2.432003000	0.904835000	-1.896979000
C	4.726094000	-0.091123000	1.073832000
H	3.027735000	-1.201831000	1.809298000
C	5.215849000	0.743317000	0.063591000
H	4.763984000	1.751782000	-1.791477000
H	5.367042000	-0.374734000	1.904604000
H	6.238416000	1.109160000	0.107234000
C	-2.586774000	-0.393041000	-0.037853000
C	-2.170716000	0.907516000	0.260183000
C	-3.950676000	-0.683809000	-0.181178000
C	-3.126191000	1.916548000	0.413058000
H	-1.113916000	1.129245000	0.371376000
C	-4.894962000	0.331669000	-0.023387000
H	-4.274219000	-1.695128000	-0.416767000
C	-4.487660000	1.636217000	0.273713000
H	-2.798228000	2.926967000	0.644424000
H	-5.951180000	0.100573000	-0.135989000
H	-5.224653000	2.425470000	0.394493000

Figure S1. Absorption UV-vis spectra changes upon irradiation (λ = 266 nm) of PT in acetonitrile.

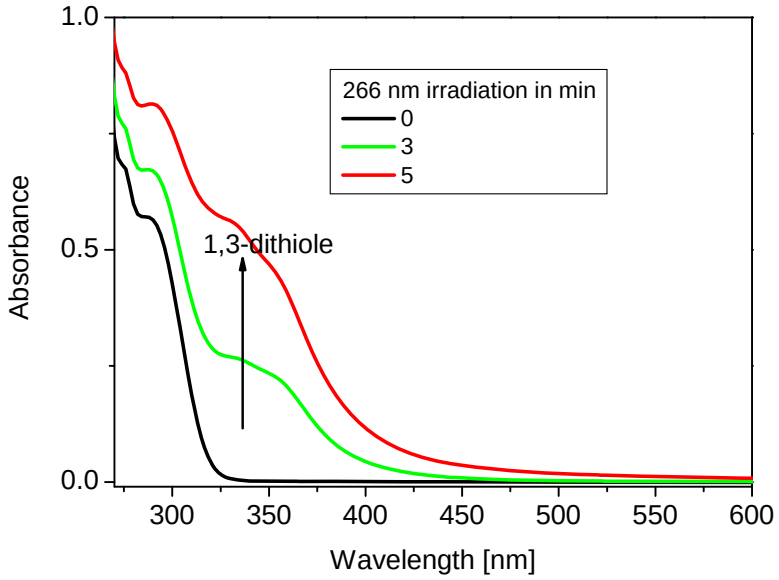
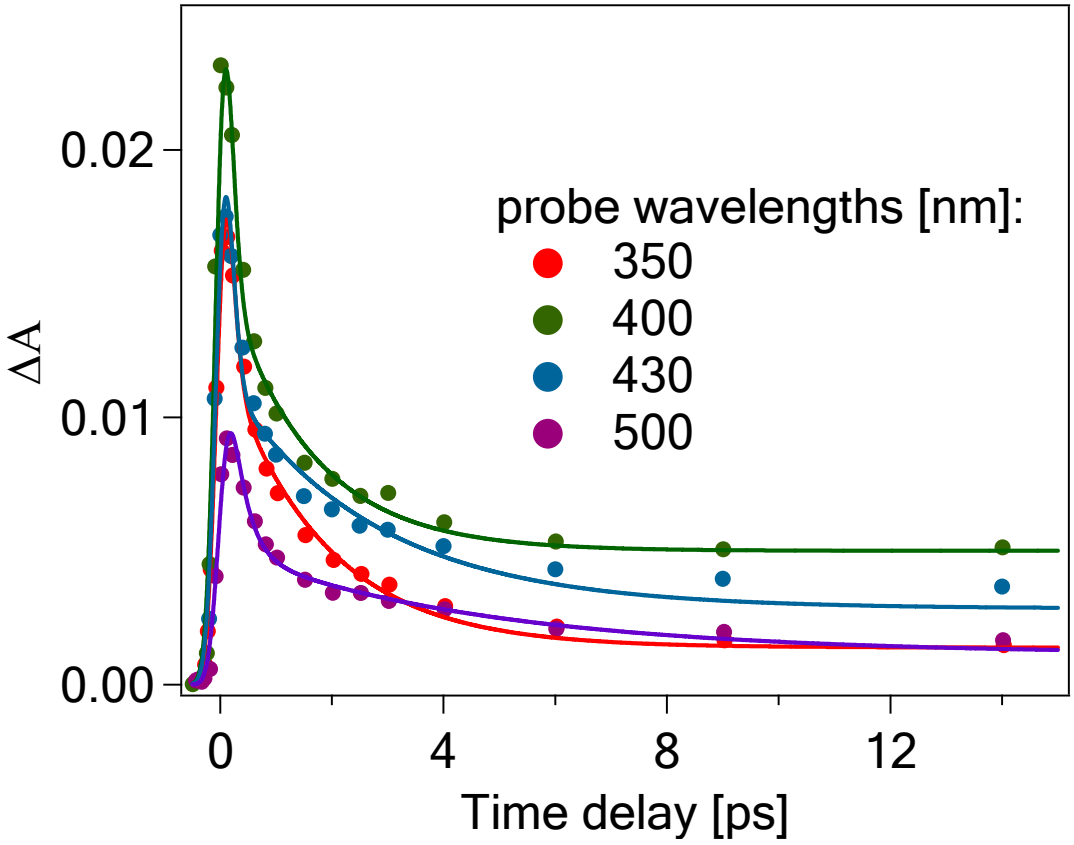
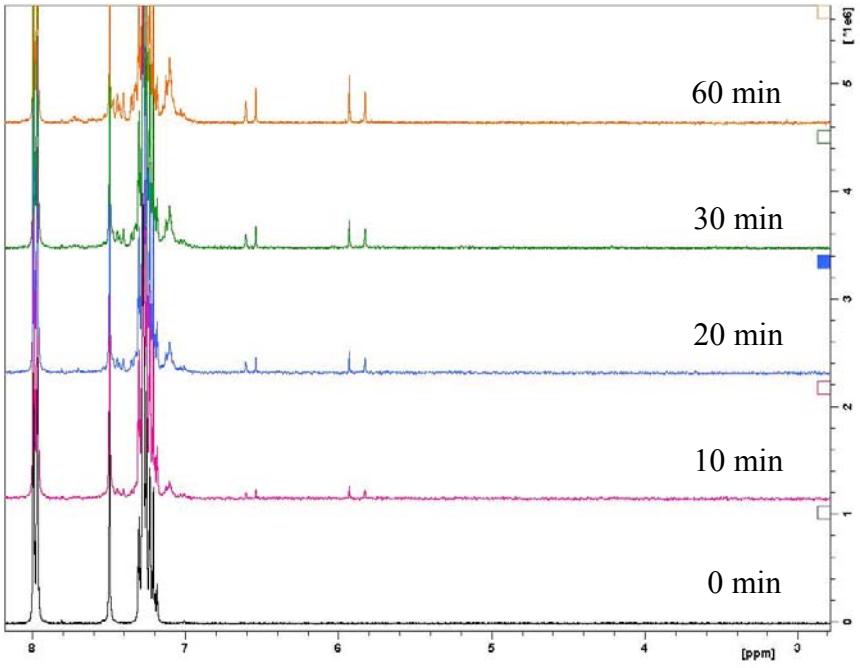


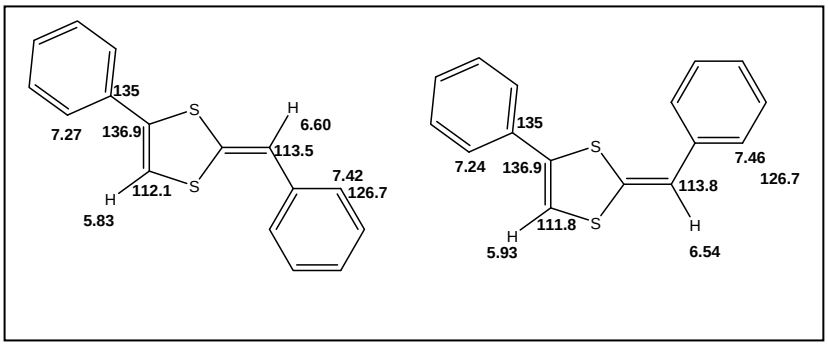
Figure S2. Transient absorption results were recorded for PT in acetonitrile with excitation at 266 nm. Kinetic traces at 350, 400, 430 and 500 nm (points) fitted to a double exponential function (solid lines).



Probe [nm]	A_1	τ_1[ps]	A_2	τ_2 [ps]	Offset
350	0.044	0,08	0.011	1.8	0.001
400	0.066	0.07	0.011	1.50	0.005
430	0.055	0.07	0.009	2.6	0.003
500	0.011	0.26	0.004	4.7	0.001

Figure S3. 1H NMR spectrum of PT in deuterated benzene after irradiation (λ = 254 nm).





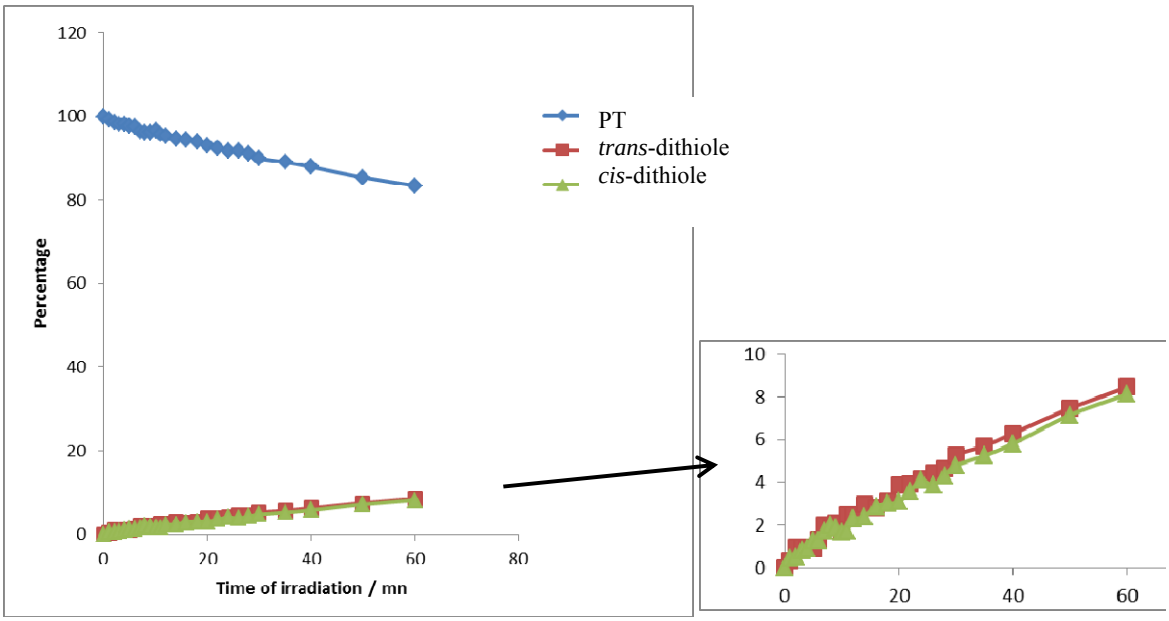


Figure S4. Determined IR absorption spectrum of 1,3-dithiole derivatives (trans and cis) in deuterated acetonitrile, formed upon irradiation of PT at 266 nm. Vertical bars denote calculated IR transitions of 1,3-dithioles.

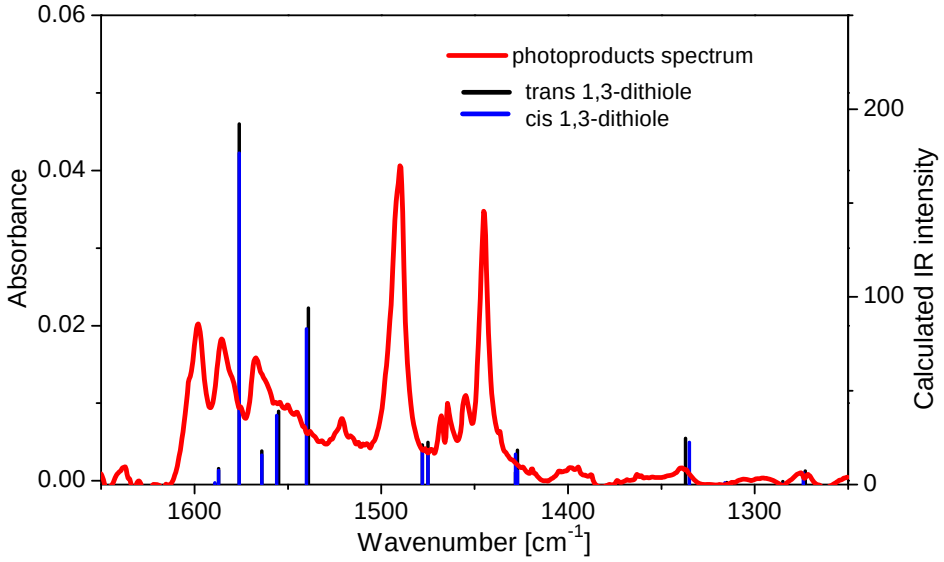
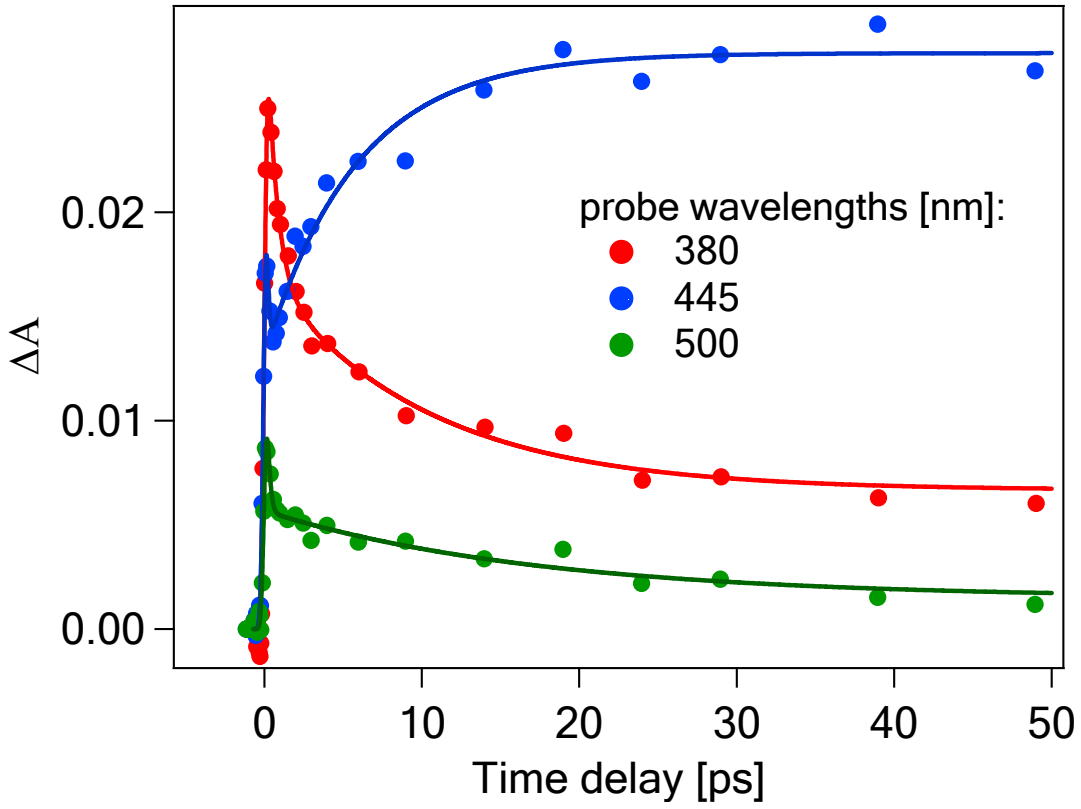


Figure S5. Transient absorption results recorded for DPT in acetonitrile with excitation at 266 nm. Kinetic traces at 380, 445 and 500 nm (points) fitted to a double exponential function (solid lines).



Probe [nm]	A_1	τ_1 [ps]	A_2	τ_2[ps]	Offset
380	0.015	0.65	0.010	10.2	0.007
445	0.056	0.06	-0.015	5.8	0.028
500	0.016	0.14	0.004	17	0.001

Figure S6. Absorption UV-vis spectrum of diphenyl-acetylene (solid blue curve) and tetraphenyl-thiophene (red curve) in acetonitrile.

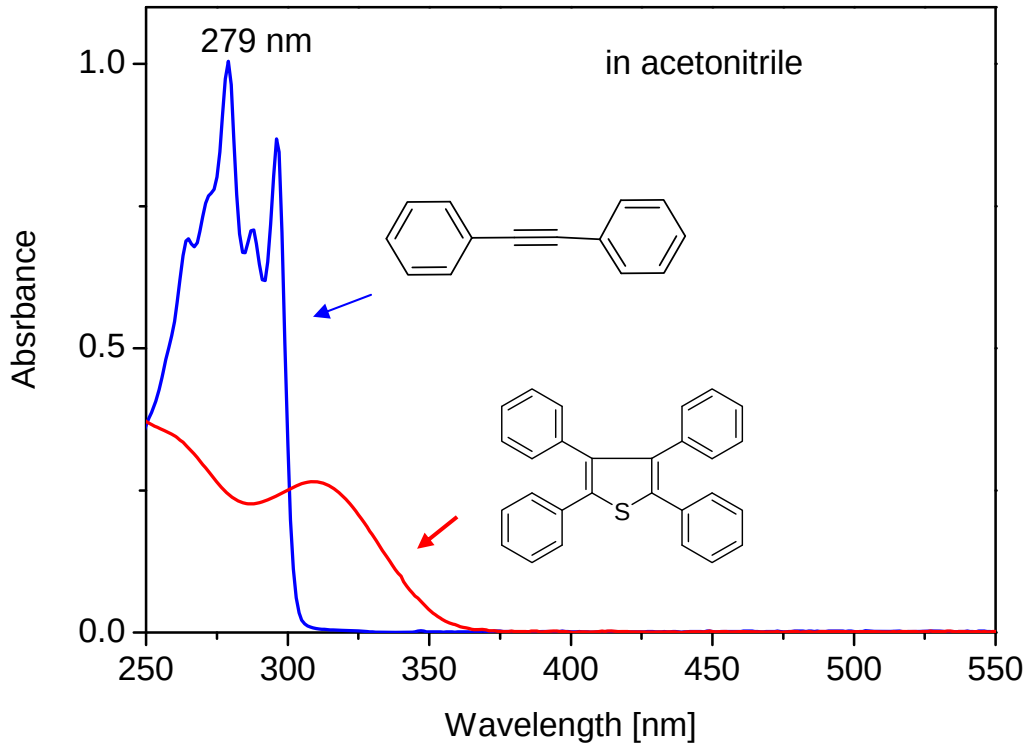


Figure S7. IR absorption spectrum of authentic samples: tetraphenyl-thiophene in CCl_4 (in ACN-d_3 solubility too low) and diphenylacetylene in ACN-d_3. Determined photoproducts IR spectrum (shown as a negative spectrum for clarity) for irradiated solution of DPT in ACN-d_3 (λ = 266 nm).

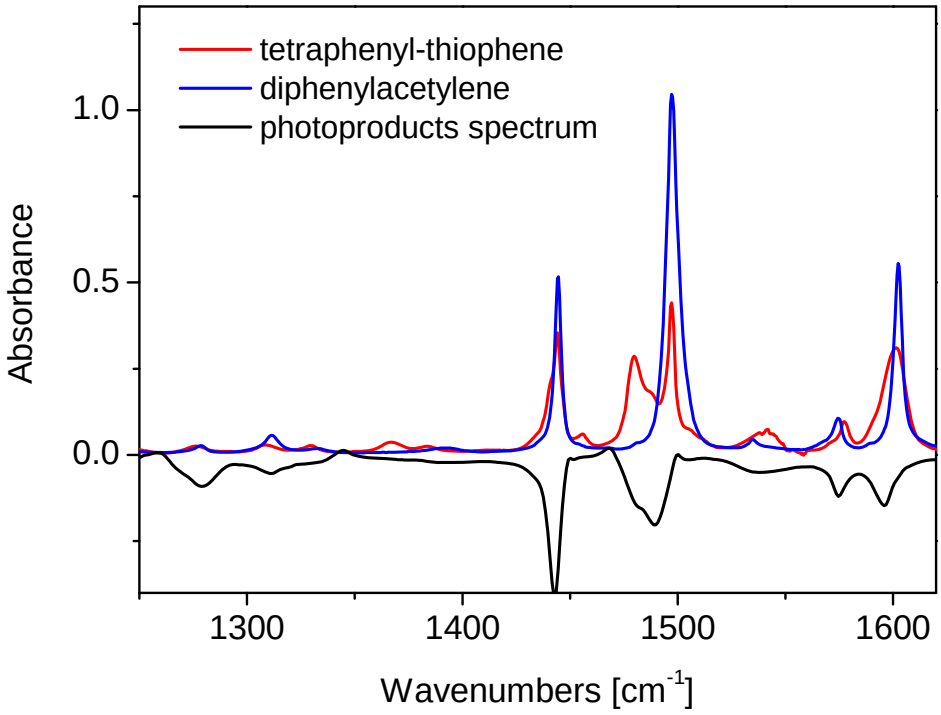
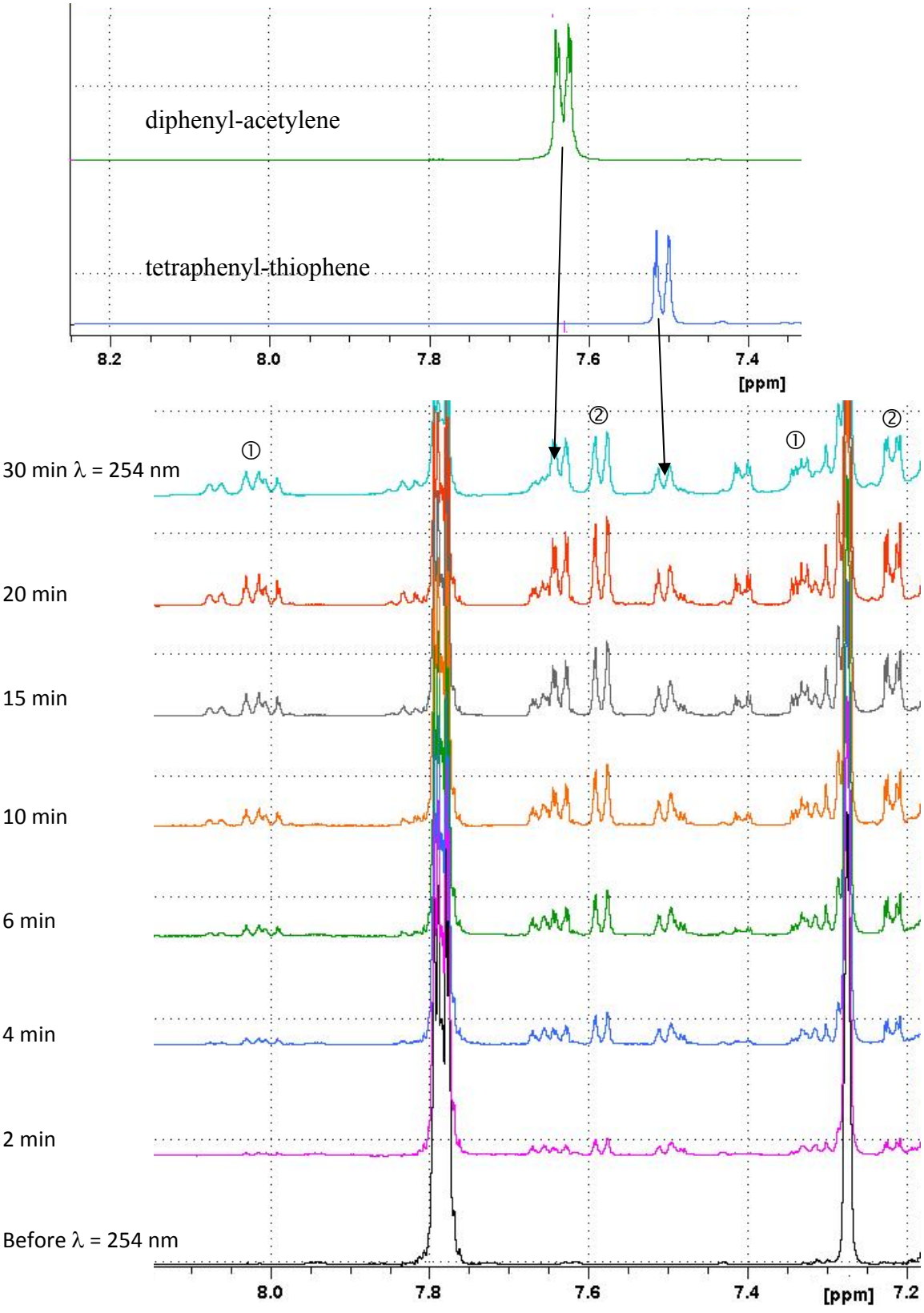


Figure S8. 1H NMR spectrum of authentic samples (diphenyl-acetylene, tetraphenyl-thiophene) and DPT in deuterated benzene after irradiation at λ = 254 nm.



presumably: ① - phenyl(2-phenylethynyl)sulfane, ② - 1,3-dithiole,

Figure S9. Time-resolved infrared transient absorption spectra produced in CH_3OD after photoexcitation of DPT at 266 nm.