

**Supplementary Data for**  
**Modeling Ultrafast Deactivation in Oligothiophenes**  
**via Nonadiabatic Dynamics**

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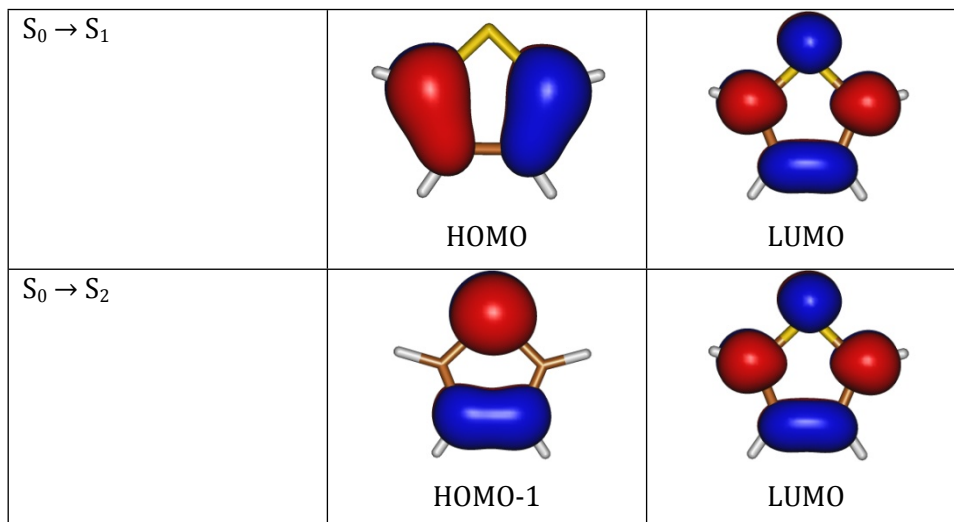
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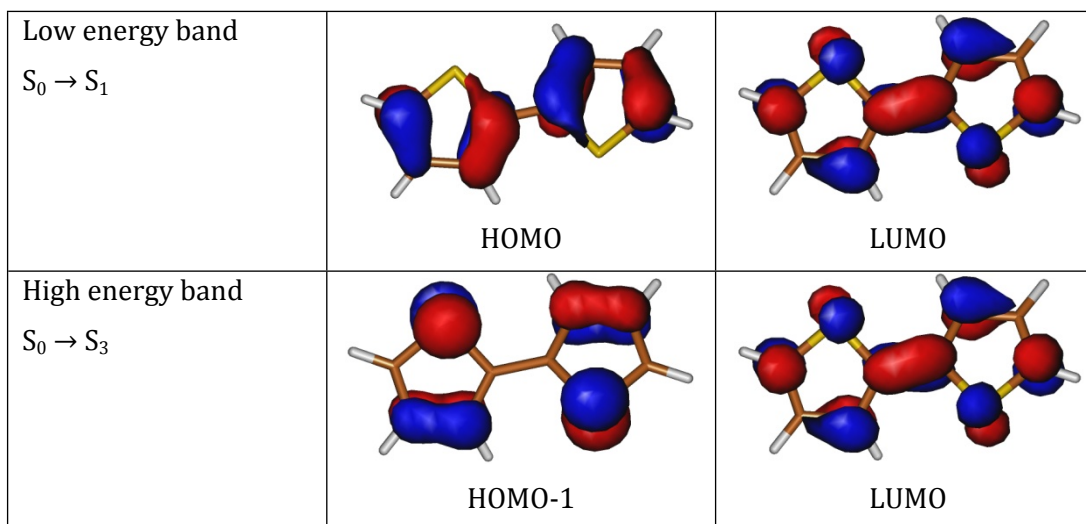
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**S1. Kohn-Sham orbitals (MOs) involved in the main electronic transitions for 1T, 2T, 3T, and 4T.**

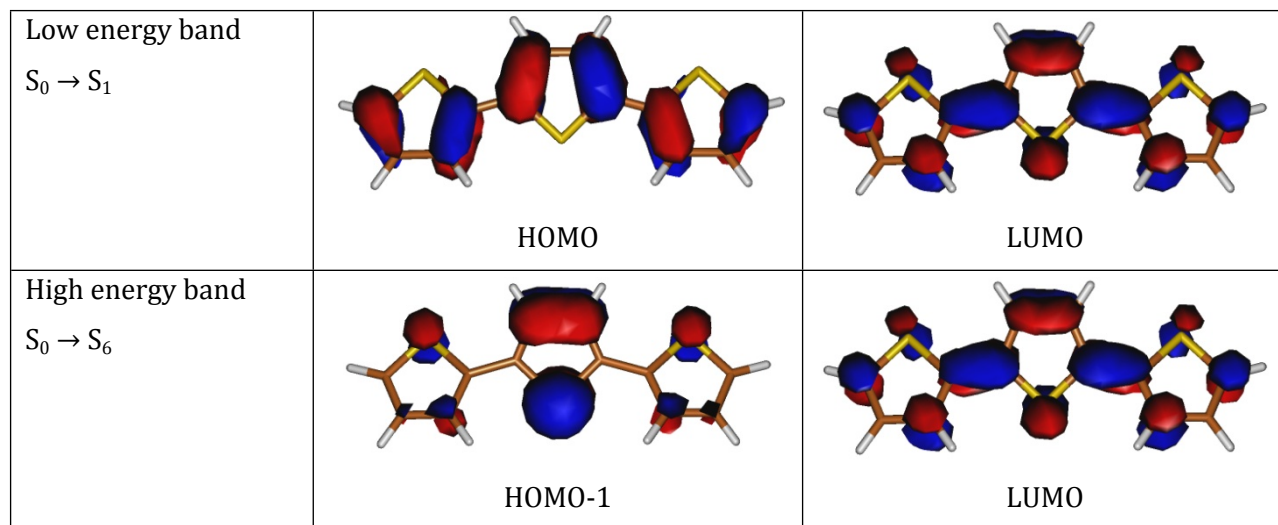
**Figure S1.1** 1T - DFT ( $\omega$ B97XD/6-31G\*) orbitals involved in  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  transitions.



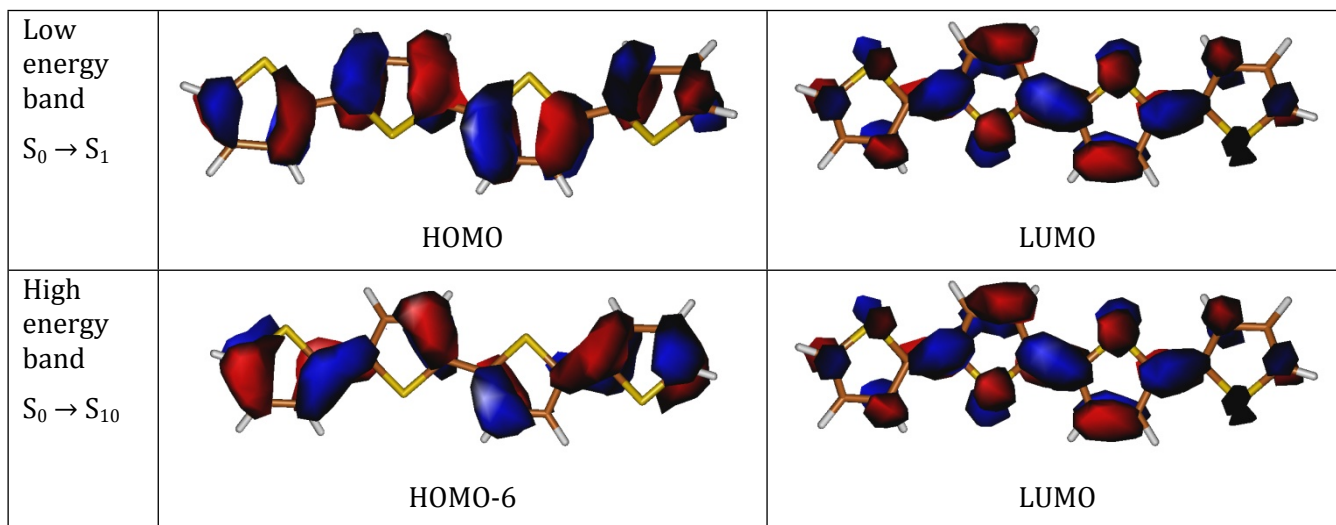
**Figure S1.2** 2T - DFT ( $\omega$ B97XD/6-31G\*) orbitals involved in low-energy band ( $S_0 \rightarrow S_1$ ) and high-energy band ( $S_0 \rightarrow S_3$ ) transitions.



**Figure S1.3** 3T - DFT ( $\omega$ B97XD/6-31G\*) orbitals involved in low-energy band ( $S_0 \rightarrow S_1$ ) and high-energy band ( $S_0 \rightarrow S_6$ ) transitions.



**Figure S1.4** 4T - DFT ( $\omega$ B97XD/6-31G\*) orbitals involved in low-energy band ( $S_0 \rightarrow S_1$ ) and high-energy band ( $S_0 \rightarrow S_{10}$ ) transitions.



## S2. Thiophene ring (1T): optimized ground- and excited-state geometries.

The optimized Cartesian coordinates for thiophene in the ground electronic state  $S_0$  and the first excited state  $S_1$  are reported in this section.

TDDFT vs. TDA methods are considered, using  $\omega$ B97XD and B3LYP functionals, with the 6-31G\* and 6-311+G\* basis sets.

In some cases, although restrictive optimization criteria were used, it was not possible to optimize the stable equilibrium armchair structure of 1T in  $S_1$ , resulting instead in a ring-opened structure.

The optimized TDDFT and TDA structures are comparable to those obtained in previous studies [see Salzmann S. et al., *Phys. Chem. Chem. Phys.*, **2008**, *10*, 380 and Stenrup M., *Chem. Phys.*, **2012**, *397*, 18].

XYZ format in Angstrom.

### $\omega$ B97XD/6-31G\* - $S_0$

S	0.000000	1.192685	0.000000
C	1.237296	-0.008625	0.000000
C	0.713548	-1.267517	0.000000
C	-0.713772	-1.267466	0.000000
C	-1.236952	-0.008600	0.000000
H	2.279067	0.280785	0.000000
H	1.319826	-2.165766	0.000000
H	-1.320853	-2.165283	0.000000
H	-2.278765	0.280547	0.000000

E = -552.928380054 Hartree

### TDDFT $\omega$ B97XD/6-31G\* - $S_1$ (armchair geometry)

C	-0.003160	-0.080043	0.046637
S	0.000190	-0.575724	1.734078
C	1.676060	-0.074362	1.781714
C	2.282901	-0.136636	0.469469
C	1.325843	-0.123497	-0.512876
H	2.044657	0.571080	2.579911
H	3.353192	-0.065432	0.311528
H	1.513645	-0.035475	-1.577322
H	-0.813773	0.520089	-0.366815

E = -552.735242913 Hartree

### TDA $\omega$ B97XD/6-31G\* - $S_1$ (ring opening geometry)

C	1.058538	1.265630	-0.000224
S	-1.404739	0.412033	0.000071
C	-0.558725	-1.018303	-0.000116
C	0.841880	-1.099368	-0.000077
C	1.660067	0.064300	0.000179
H	-1.118778	-1.952404	0.000102
H	1.300984	-2.085049	-0.000365
H	2.746330	-0.071919	0.000804
H	1.536732	2.243290	-0.000249

E = -552.765264108 Hartree

**$\omega$ B97XD/6-311+G\* - S<sub>0</sub>**

S	0.000000	1.191427	0.000000
C	1.234594	-0.008565	0.000000
C	0.712543	-1.266564	0.000000
C	-0.712767	-1.266494	0.000000
C	-1.234249	-0.008526	0.000000
H	2.274966	0.282277	0.000000
H	1.319380	-2.163317	0.000000
H	-1.320377	-2.162846	0.000000
H	-2.274694	0.281953	0.000000

E = -552.986322335 Hartree

**TDDFT  $\omega$ B97XD/6-311+G\* - S<sub>1</sub> (armchair geometry)**

C	0.002107	-0.068471	0.049461
S	-0.004211	-0.563188	1.729245
C	1.671182	-0.056345	1.772576
C	2.279750	-0.122186	0.465923
C	1.327908	-0.128960	-0.516667
H	2.056272	0.533929	2.602181
H	3.349177	-0.047231	0.310746
H	1.516448	-0.060462	-1.581158
H	-0.819078	0.512913	-0.365981

E = -552.798466682 Hartree

**TDA  $\omega$ B97XD/6-311+G\* - S<sub>1</sub> (ring opening geometry)**

C	1.075382	1.261915	0.000313
S	-1.401931	0.418546	-0.000162
C	-0.567124	-1.012997	0.000223
C	0.831359	-1.103113	0.000202
C	1.655901	0.052939	-0.000566
H	-1.134991	-1.941228	0.000290
H	1.283655	-2.090878	0.000924
H	2.741034	-0.088611	-0.001430
H	1.568094	2.231527	0.001775

E = -552.824567546 Hartree

**B3LYP /6-31G\* - S<sub>0</sub>**

S	0.000000	1.199370	0.000000
C	1.243725	-0.011263	0.000000
C	0.714556	-1.272695	0.000000
C	-0.714753	-1.272558	0.000000
C	-1.243363	-0.011223	0.000000
H	2.285143	0.280907	0.000000
H	1.319592	-2.172991	0.000000
H	-1.320933	-2.172226	0.000000
H	-2.284788	0.280823	0.000000

E = -553.002627818 Hartree

**TDDFT B3LYP /6-31G\* - S<sub>1</sub> (ring opening geometry)**

C	1.143066	1.265225	-0.000028
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S	-1.431586	0.433905	0.000038
C	-0.585668	-1.007279	-0.000068
C	0.820535	-1.110448	0.000063
C	1.679205	0.028453	0.000038
H	-1.154209	-1.937097	-0.000414
H	1.256213	-2.107829	0.000051
H	2.760140	-0.156804	0.000059
H	1.700394	2.203556	-0.000332

E = -552.885802460 Hartree

**TDA B3LYP /6-31G\* - S1 (ring opening geometry)**

S	-1.448346	-0.329361	0.000000
C	0.343348	1.649940	0.000000
C	1.434123	0.862699	0.000000
C	1.269170	-0.556964	0.000000
C	0.000000	-1.166811	0.000000
H	0.323474	2.740188	0.000000
H	2.459062	1.253098	0.000000
H	2.146509	-1.200785	0.000000
H	-0.035358	-2.255914	0.000000

E = -552.855540747 Hartree

**B3LYP /6-311+G\* - S<sub>0</sub>**

S	0.000000	-1.198149	0.000000
C	-1.240965	0.011197	0.000000
C	-0.713581	1.271811	0.000000
C	0.713769	1.271658	0.000000
C	1.240614	0.011169	0.000000
H	-2.280450	-0.281982	0.000000
H	-1.319011	2.169934	0.000000
H	1.320298	2.169195	0.000000
H	2.280143	-0.281770	0.000000

E = -553.065521820 Hartree

**TDDFT B3LYP /6-311+G\* - S<sub>1</sub> (ring opening geometry)**

S	-1.445483	-0.332507	0.000000
C	0.345198	1.654400	0.000000
C	1.428986	0.862404	0.000000
C	1.266526	-0.555565	0.000000
C	0.000000	-1.166099	0.000000
H	0.326412	2.742918	0.000000
H	2.451154	1.256656	0.000000
H	2.143662	-1.197010	0.000000
H	-0.037759	-2.253284	0.000000

E = -552.919678032 Hartree

### S3. Thiophene ring (1T): relaxed potential energy profiles along $S_1$ surface.

TDDFT relaxed potential energy profiles in  $S_1$  along the C-S bond elongation coordinate were computed.

Starting from the flat ring structure (equilibrium in the ground state), at the TDDFT( $\omega$ B97XD)/6-31G\* level, we first obtained a ring puckered geometry (stable structure in  $S_1$ ), and consequently a decrease of the  $S_1$  energy with an increase of  $S_0$  until reaching the  $S_1/S_0$  crossing with a ring opening structure.

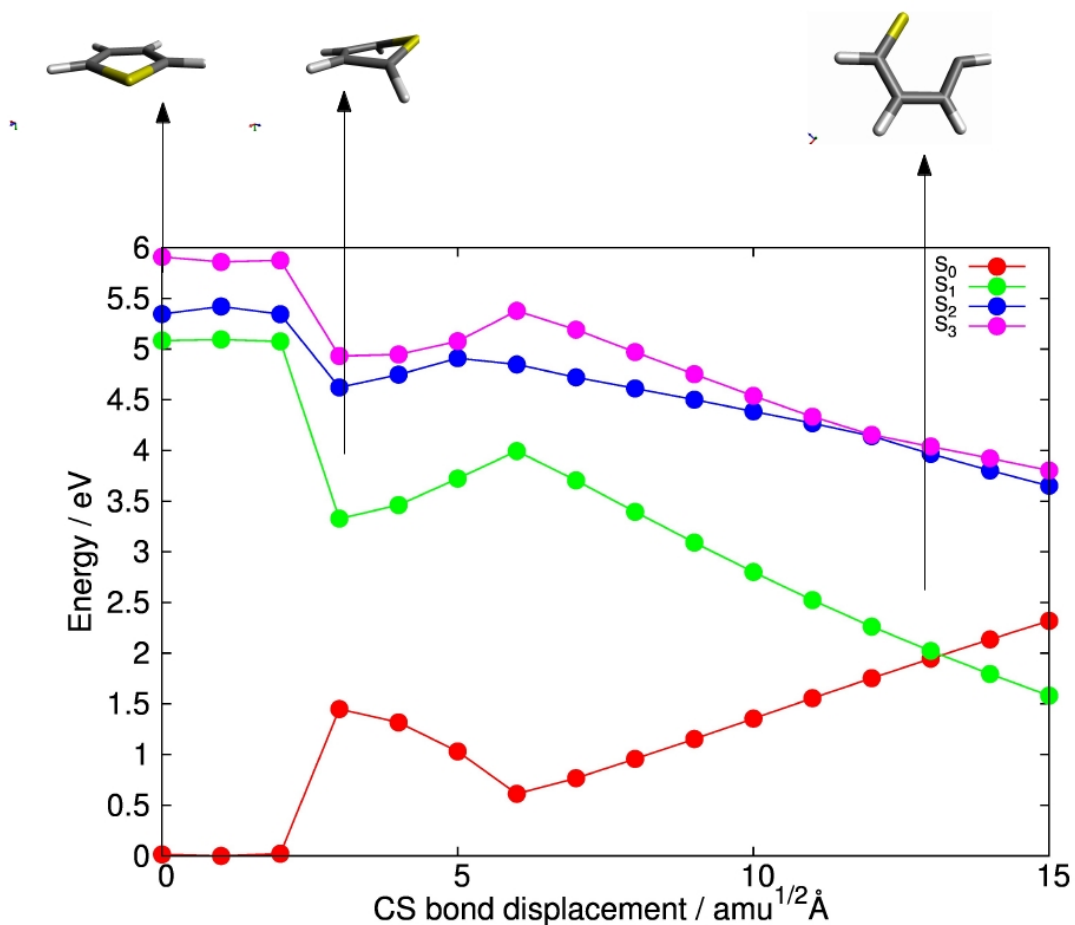
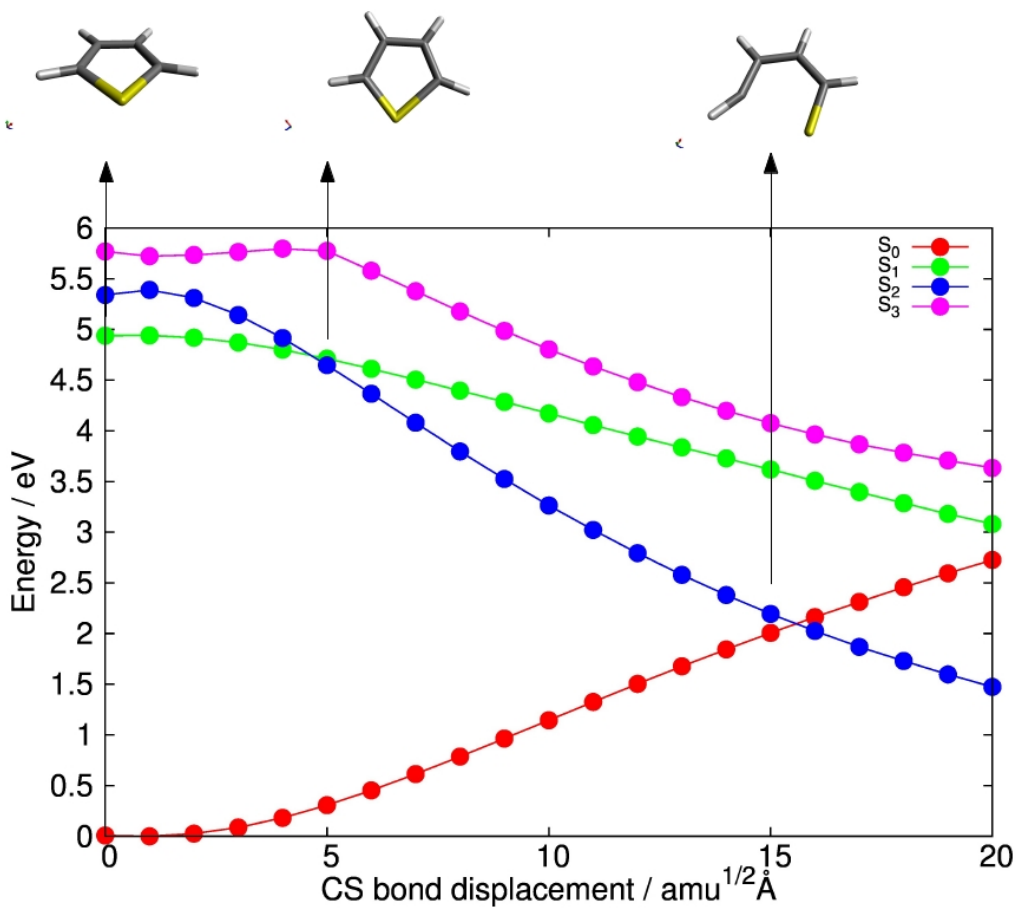


Figure S3.1: TDDFT  $\omega$ B97XD/6-31G\* potential energy profile along the C-S stretching coordinate for 1T.

In the case of TDDFT( $\omega$ B97XD)/6-311+G\*, a crossing between  $S_2$  and  $S_1$  occurs as soon as we elongate the C-S bond. Similarly to TDDFT( $\omega$ B97XD)/6-31G\*, a stabilization of  $S_2$  and an energy increase of  $S_0$  occurs until the crossing (ring opening structure).

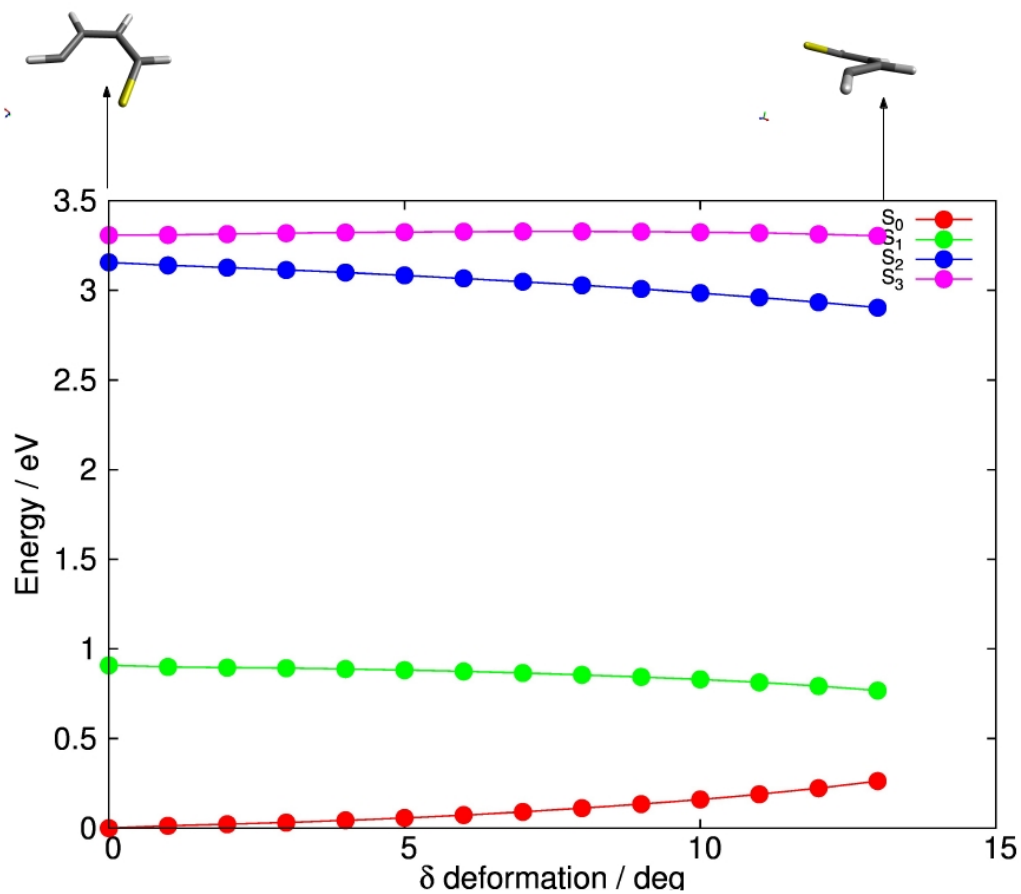


**Figure S3.2:** TDDFT  $\omega$ B97XD/6-311+G\* potential energy profile along the C-S stretching coordinate for 1T.



We also tried to run a relaxed scan in  $S_1$  along the puckering coordinate ( $\delta$ ), thus increasing the C-C-C-S dihedral angle. Already at the first step, the relaxed structure is the ring opening geometry, featuring a very low energy with respect to the closed one. From this geometry, the scan proceeded with a further stabilization of  $S_1$  and destabilization of  $S_0$ .

As an example, we report the TDDFT( $\omega$ B97XD)/6-311+G\* result below.

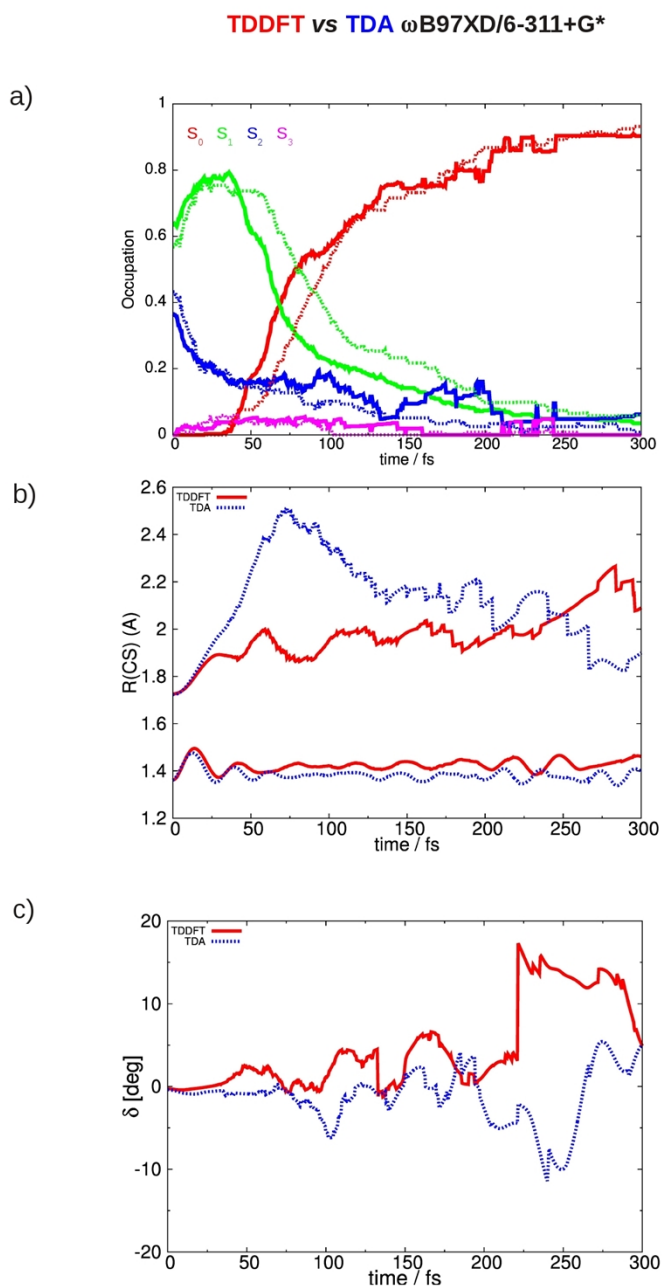


**Figure S3.3:** TDDFT  $\omega$ B97XD/6-311+G\* potential energy profile along the puckering coordinate for 1T.

#### S4. TDDFT vs. TDA nonadiabatic excited state dynamics ( $\omega$ B97XD).

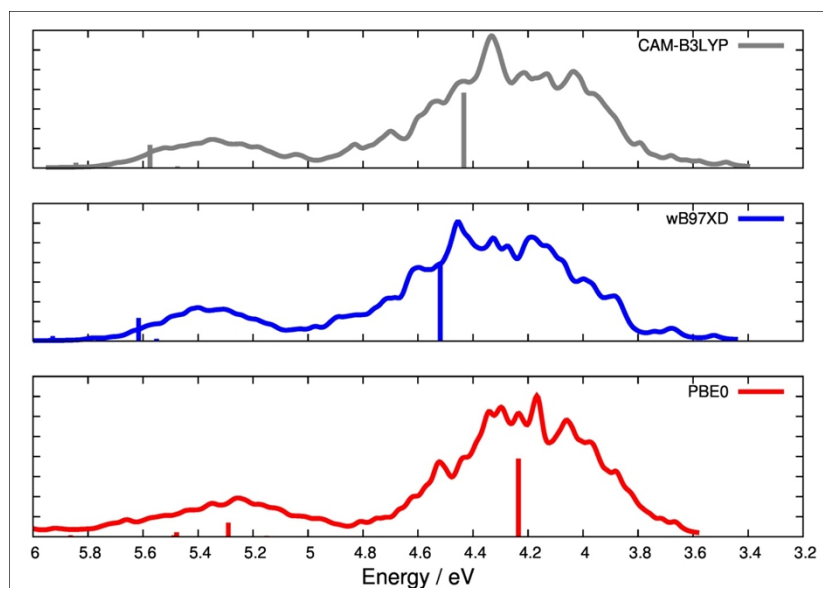
In this section, we summarize the results from TDDFT and TDA nonadiabatic excited-state dynamics of 1T at the  $\omega$ B97XD/6-311+G\* level.

In Panel a), the fraction of trajectories vs. time are reported. The  $S_1$  decay time constant computed at TDDFT is  $\tau_1 = 85$  fs, and the  $S_0$  occupation time constant is  $\tau_0 = 103$  fs. For TDA we obtained  $\tau_1 = 115$  fs and  $\tau_0 = 135$  fs. In panels b) and c), we report the C-S bond lengths vs. time and the ring puckering angle vs. time. As discussed in the paper for the 6-31G\* case, an initial ultrafast huge elongation of the C-S bond occurs within 70 fs concomitantly with a decrease of the  $S_1$  population (ca. 50 %).



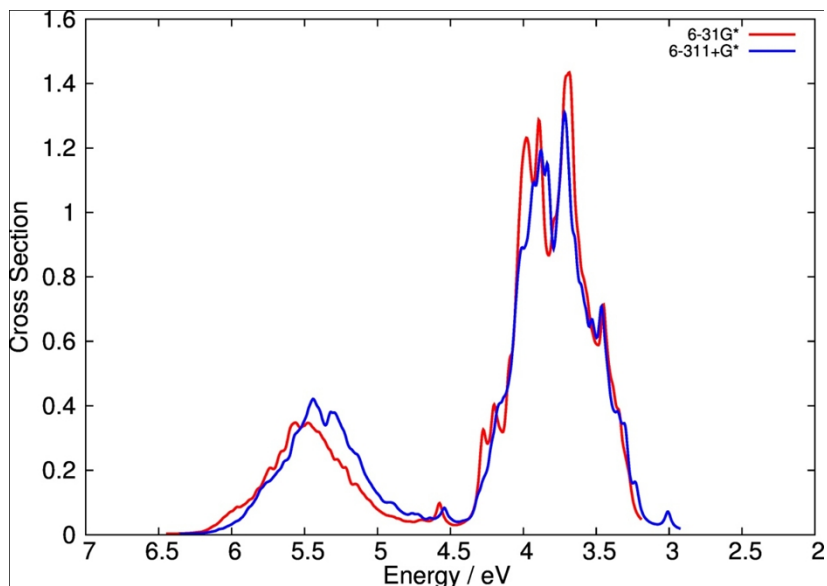
**Figure S4.1:** TDDFT and TDA  $\omega$ B97XD/6-311+G\* nonadiabatic excited-state dynamics. Panel a) fraction of trajectories vs. time. Panel b) C-S bond lengths vs. time. Panel c) Puckering coordinate vs. time. Red line TDDFT results, blue dotted line TDA.

## S5. TDDFT absorption cross section of bithiophene.

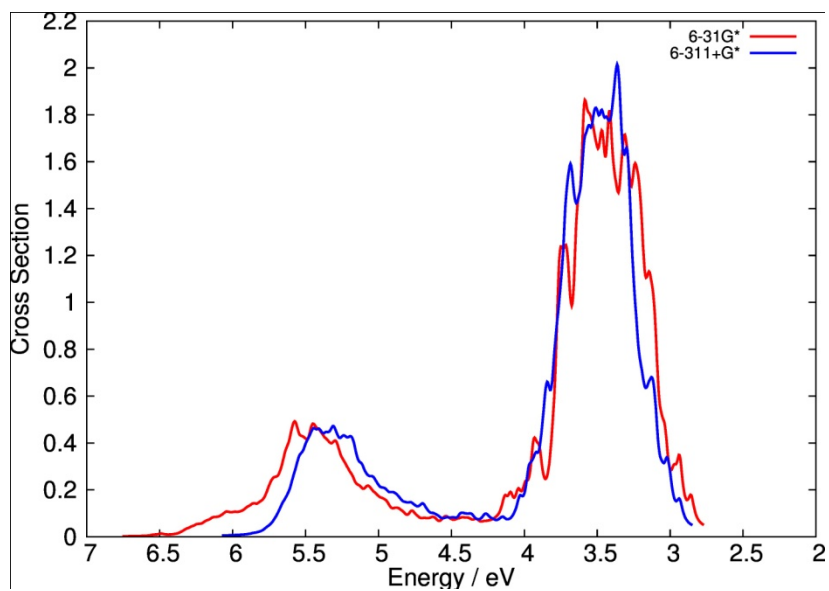


**Figure S6.1:** TDDFT PBE0 (red),  $\omega$ B97XD (blue), and CAM-B3LYP (grey) 6-311+G\* absorption cross section ( $\text{\AA}^2/\text{molecule}$ ) computed with the nuclear ensemble method for 2T.

**S6. TDDFT absorption cross section of 3T and 4T (comparison between  $\omega$ B97XD/6-31G\* and 6-311+G\*). Comparison between  $\omega$ B97XD and B3LYP/6-31G\* on the vertical transition energies for low and high energy dipole allowed excited states.**



**Figure S6.1:** TDDFT  $\omega$ B97XD 6-31G\* (red) and 6-311+G\* (blue) absorption cross section ( $\text{\AA}^2/\text{molecule}$ ) computed with the nuclear ensemble method for 3T.



**Figure S6.2:** TDDFT  $\omega$ B97XD 6-31G\* (red) and 6-311+G\* (blue) absorption cross section ( $\text{\AA}^2/\text{molecule}$ ) computed with the nuclear ensemble method for 4T.

**Table S6.3** Comparison between  $\omega$ B97XD and B3LYP/6-31G\* for  $S_1$  (bright state) and  $S_n$  (high energy excited state responsible of the second absorption band).

	<i><math>\omega</math>B97XD</i>	<i>B3LYP</i>
	<i>E /eV (Oscillator Strength)</i>	<i>E /eV (Oscillator Strength)</i>
$S_1$	3.62 (1.1978)	2.92 (1.2021)
$S_n$	5.67 (0.1494)	5.09 (0.0731)

### S7. Oligothiophenes ( $nT$ , $n = 2,3,4$ ): optimized ground- and excited-state geometries.

For the case of 2T,  $\omega$ B97XD with 6-31G\* and 6-311+G\* were considered. Structures with CAM-B3LYP and PBE0 using 6-311+G\* are also reported.

XYZ format in Ångstrom.

#### 2T

##### $\omega$ B97XD/6-31G\* - $S_0$

S	1.825111	1.167383	-0.302608
C	3.189419	0.139029	-0.071577
C	2.814205	-1.125487	0.271425
C	1.400839	-1.272213	0.365886
C	0.719167	-0.115706	0.090453
C	-0.719170	0.115703	0.090394
S	-1.825102	-1.167339	-0.302860
C	-3.189433	-0.139169	-0.071152
C	-2.814211	1.125471	0.271383
C	-1.400835	1.272278	0.365559
H	-4.189805	-0.527594	-0.203234
H	-3.518831	1.926385	0.461435
H	-0.905004	2.194116	0.648571
H	4.189780	0.527348	-0.204050
H	3.518820	-1.926411	0.461448
H	0.905017	-2.193999	0.649087

E = -1104.67220627 Hartree

##### TDDFT $\omega$ B97XD/6-31G\* - $S_1$

S	1.819137	1.265476	0.157248
C	3.161943	0.180360	0.157279
C	2.777340	-1.156261	0.157422
C	1.400646	-1.344468	0.157757
C	0.682411	-0.109388	0.157654
C	-0.682414	0.109367	0.157696
S	-1.819138	-1.265500	0.157671
C	-3.161945	-0.180388	0.157600
C	-2.777346	1.156234	0.157436
C	-1.400652	1.344445	0.157612
H	-4.171127	-0.569602	0.158094
H	-3.500008	1.964157	0.157334
H	-0.902312	2.306792	0.156975
H	4.171126	0.569572	0.157611
H	3.500001	-1.964186	0.157417
H	0.902303	-2.306814	0.157354

E = -1104.52574136 Hartree

##### $\omega$ B97XD/6-311+G\* - $S_0$

S	1.817706	1.152641	-0.350627
C	3.184113	0.141053	-0.080524
C	2.815207	-1.107723	0.316226
C	1.404309	-1.254083	0.421934
C	0.719444	-0.113873	0.101449
C	-0.719436	0.113890	0.101472
S	-1.817730	-1.152693	-0.350329

C	-3.184122	-0.141090	-0.080209
C	-2.815187	1.107766	0.316261
C	-1.404276	1.254173	0.421749
H	-4.181212	-0.527997	-0.232501
H	-3.523522	1.896049	0.537871
H	-0.913339	2.163328	0.747245
H	4.181190	0.527913	-0.233018
H	3.523557	-1.895976	0.537892
H	0.913398	-2.163172	0.747653

E = -1104.78571985 Hartree

**TDDFT  $\omega$ B97XD/6-311+G\* - S<sub>1</sub>**

S	1.837036	1.231819	-0.000279
C	3.157132	0.124650	-0.000346
C	2.751457	-1.204283	-0.000012
C	1.373694	-1.367544	0.000342
C	0.678721	-0.120324	0.000100
C	-0.678721	0.120326	0.000137
S	-1.837035	-1.231819	0.000135
C	-3.157132	-0.124652	-0.000030
C	-2.751458	1.204283	0.000000
C	-1.373696	1.367545	0.000194
H	-4.171594	-0.497713	0.000237
H	-3.459710	2.023462	-0.000076
H	-0.861680	2.321594	-0.000148
H	4.171594	0.497711	-0.000252
H	3.459708	-2.023464	0.000008
H	0.861678	-2.321592	0.000240

E = -1104.64410689 Hartree

**CAMB3LYP/6-311+G\* - S<sub>0</sub>**

S	-1.823408	-1.162418	-0.313947
C	-3.184477	-0.136579	-0.071719
C	-2.809900	1.120258	0.282412
C	-1.398608	1.264553	0.376955
C	-0.718259	0.115071	0.091445
C	0.718244	-0.115086	0.091594
S	1.823462	1.162562	-0.313094
C	3.184464	0.136359	-0.072016
C	2.809852	-1.120360	0.282497
C	1.398568	-1.264518	0.377373
H	4.182694	0.523431	-0.209474
H	3.512826	-1.918895	0.479961
H	0.905992	-2.182933	0.670022
H	-4.182708	-0.523802	-0.208751
H	-3.512907	1.918716	0.480066
H	-0.906055	2.182992	0.669567

E = -1104.74275394 Hartree

**PBE0/6-311+G\* - S<sub>0</sub>**

S	1.825111	1.167383	-0.302608
C	3.189419	0.139029	-0.071577
C	2.814205	-1.125487	0.271425
C	1.400839	-1.272213	0.365886

C	0.719167	-0.115706	0.090453
C	-0.719170	0.115703	0.090394
S	-1.825102	-1.167339	-0.302860
C	-3.189433	-0.139169	-0.071152
C	-2.814211	1.125471	0.271383
C	-1.400835	1.272278	0.365559
H	-4.189805	-0.527594	-0.203234
H	-3.518831	1.926385	0.461435
H	-0.905004	2.194116	0.648571
H	4.189780	0.527349	-0.204050
H	3.518820	-1.926411	0.461448
H	0.905017	-2.193999	0.649087

E = -1104.26161434 Hartree

### 3T

#### $\omega$ B97XD/6-31G\* - S<sub>0</sub>

C	-3.218482	1.372723	0.225266
C	-4.633024	1.364867	0.065707
C	-5.126727	0.119445	-0.184325
S	-3.873227	-1.062434	-0.247794
C	-2.653899	0.130730	0.091434
C	-1.251907	-0.245052	0.192181
S	0.000018	0.897023	-0.197994
C	1.251925	-0.245071	0.192182
C	0.709759	-1.446665	0.566600
C	-0.709760	-1.446654	0.566602
H	-1.311801	-2.297472	0.865618
H	1.311787	-2.297493	0.865616
H	-2.640873	2.261476	0.454181
H	-5.253847	2.249480	0.143324
H	-6.156413	-0.171951	-0.338803
C	2.653924	0.130691	0.091438
C	3.218522	1.372678	0.225258
C	4.633066	1.364802	0.065715
C	5.126754	0.119373	-0.184314
S	3.873238	-1.062489	-0.247780
H	2.640922	2.261440	0.454162

E = -1656.41660701 Hartree

#### TDDFT $\omega$ B97XD/6-31G\* - S<sub>1</sub>

C	-3.181720	1.410468	0.071314
C	-4.586480	1.389186	0.071910
C	-5.112239	0.120551	0.137892
S	-3.884797	-1.089829	0.201432
C	-2.613875	0.129059	0.138288
C	-1.258540	-0.228146	0.157158
S	-0.000001	1.006085	0.093063
C	1.258539	-0.228146	0.157158
C	0.686646	-1.528867	0.224904
C	-0.686647	-1.528867	0.224904
H	-1.295892	-2.424484	0.271474
H	1.295891	-2.424484	0.271474
H	-2.585252	2.314783	0.024402
H	-5.203172	2.279394	0.025287
H	-6.155219	-0.164723	0.152507
C	2.613874	0.129059	0.138287



C	3.181719	1.410468	0.071313
C	4.586479	1.389187	0.071908
C	5.112238	0.120551	0.137891
S	3.884797	-1.089829	0.201431
H	2.585251	2.314783	0.024401
H	5.203171	2.279395	0.025285
H	6.155218	-0.164722	0.152505

E = -1656.29216940 Hartree

### 4T

#### $\omega$ B97XD/6-31G\* - S<sub>0</sub>

S	5.773844	-1.077737	0.525074
C	7.058403	0.064581	0.398356
C	6.608938	1.286283	-0.005289
C	5.203830	1.306533	-0.232621
C	4.602372	0.097341	0.003395
C	3.197360	-0.257649	-0.124717
S	1.959250	0.942826	0.097175
C	0.696780	-0.205456	-0.238336
C	1.224803	-1.449405	-0.469981
C	2.642051	-1.478793	-0.405445
H	0.616008	-2.313069	-0.713520
H	3.234372	-2.367208	-0.593701
H	8.072458	-0.230351	0.630293
H	7.255864	2.143882	-0.146642
H	4.660032	2.177366	-0.581486
C	-0.696773	0.205451	-0.238326
C	-1.224798	1.449407	-0.469931
C	-2.642045	1.478794	-0.405378
C	-3.197352	0.257642	-0.124679
S	-1.959241	-0.942842	0.097155
C	-4.602363	-0.097349	0.003441
C	-5.203829	-1.306528	-0.232618
C	-6.608930	-1.286288	-0.005243
C	-7.058388	-0.064596	0.398442
S	-5.773824	1.077714	0.525178
H	-0.616004	2.313078	-0.713450
H	-3.234367	2.367216	-0.593600
H	-4.660039	-2.177348	-0.581529
H	-7.255859	-2.143883	-0.146609
H	-8.072438	0.230329	0.630407

E = -2208.16104254 Hartree

#### TDDFT $\omega$ B97XD/6-31G\* - S<sub>1</sub>

S	-5.809648	-1.137754	0.000303
C	-7.065815	0.043553	0.000580
C	-6.568077	1.318787	0.000534
C	-5.156159	1.361688	0.000314
C	-4.569872	0.101716	0.000140
C	-3.190290	-0.233817	-0.000100
S	-1.960038	1.014653	-0.000438
C	-0.670505	-0.188618	-0.000524
C	-1.220438	-1.494370	-0.000384
C	-2.601756	-1.509959	-0.000097
H	-0.601939	-2.384814	-0.000473

H	-3.192451	-2.419483	0.000103
H	-8.101341	-0.267812	0.000767
H	-7.198140	2.200627	0.000682
H	-4.579810	2.280245	0.000282
C	0.670505	0.188618	-0.000536
C	1.220438	1.494370	-0.000439
C	2.601756	1.509959	-0.000167
C	3.190290	0.233817	-0.000141
S	1.960038	-1.014653	-0.000430
C	4.569872	-0.101716	0.000093
C	5.156159	-1.361688	0.000296
C	6.568077	-1.318787	0.000497
C	7.065815	-0.043553	0.000498
S	5.809648	1.137754	0.000201
H	0.601939	2.384814	-0.000546
H	3.192451	2.419483	0.000001
H	4.579810	-2.280245	0.000300
H	7.198140	-2.200627	0.000662
H	8.101341	0.267812	0.000662

E = -2208.04796880 Hartree

S8. Optimized  $S_1$  potential energy profile for 2T: C-S elongation, ring puckering variation.

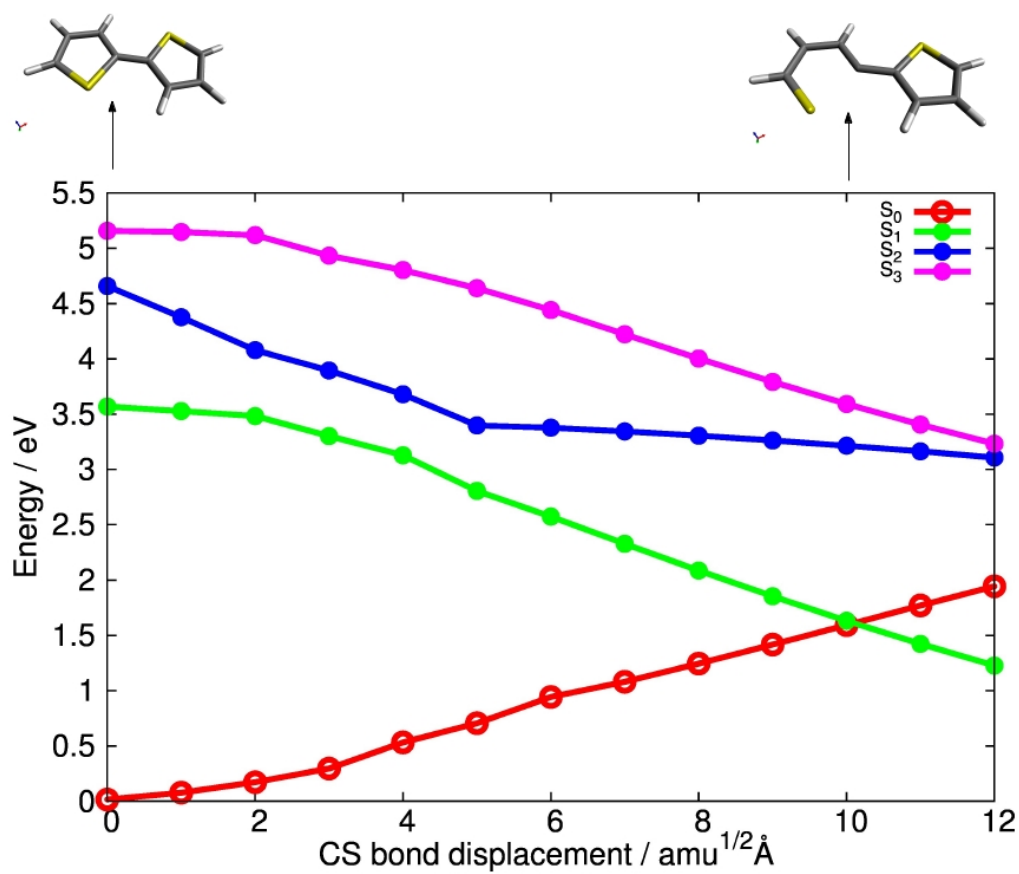
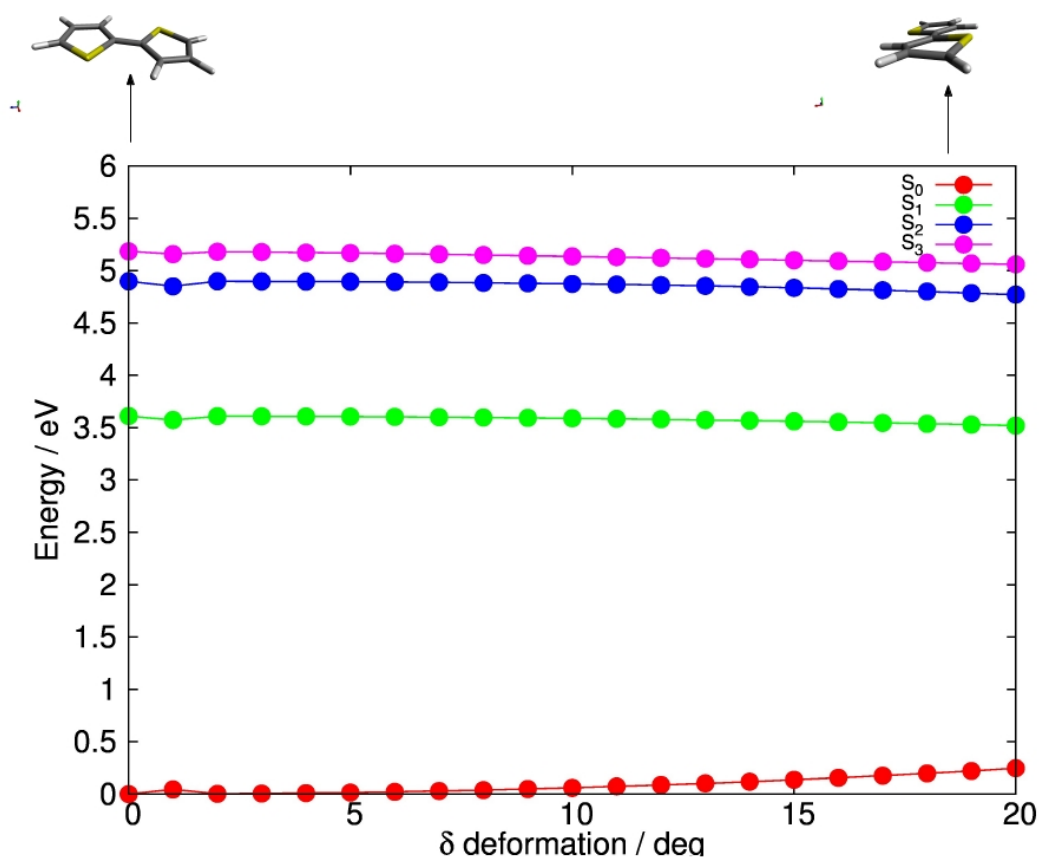
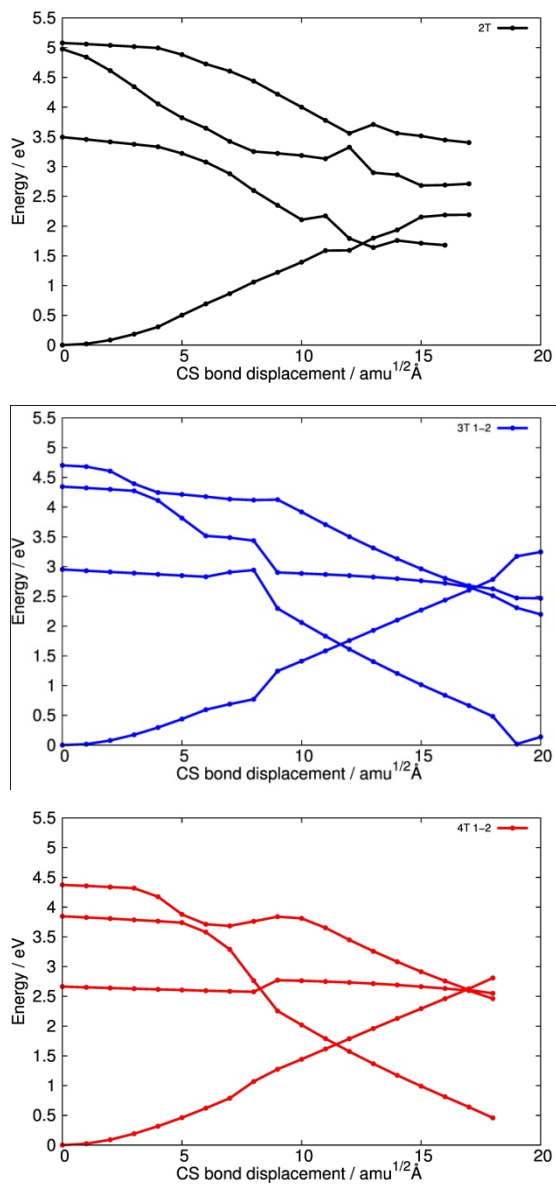


Figure S8.1: TDDFT ( $\omega$ B97XD)/6-31G\*  $S_1$  relaxed potential energy profile along the C-S stretching coordinate for 2T.



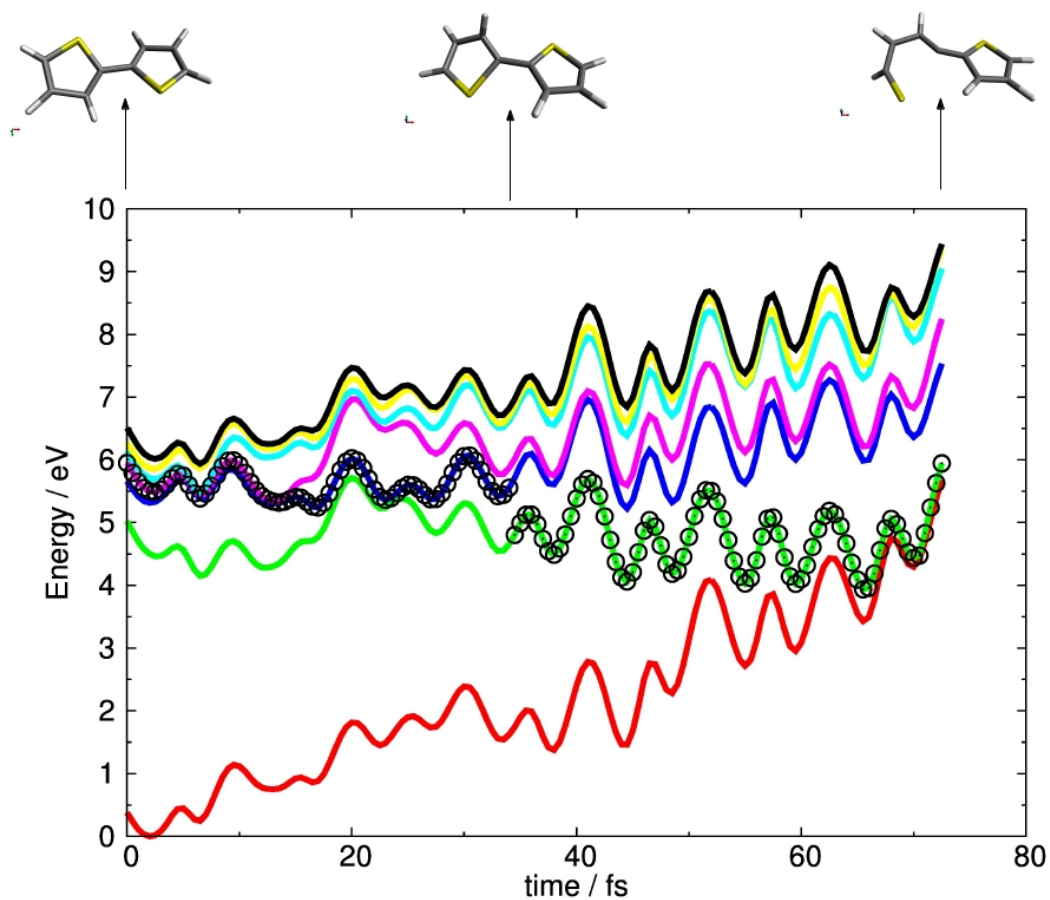
**Figure S8.2:** TDDFT ( $\omega$ B97XD)/6-31G\*  $S_1$  relaxed potential energy profile along the puckering coordinate for 2T.

S9. Optimized  $S_1$  potential energy profile: comparison between 2T, 3T and 4T.



**Figure S12.1:** TDDFT ( $\omega$ B97XD)/6-311+G\*  $S_1$  relaxed potential energy profiles along the C-S stretching coordinate for 2T (top – black lines), 3T (middle – blue line) and 4T (bottom – red lines).

**S10. Example of one TDDFT nonadiabatic excited-state dynamics trajectory from high energy excitation of 2T.**



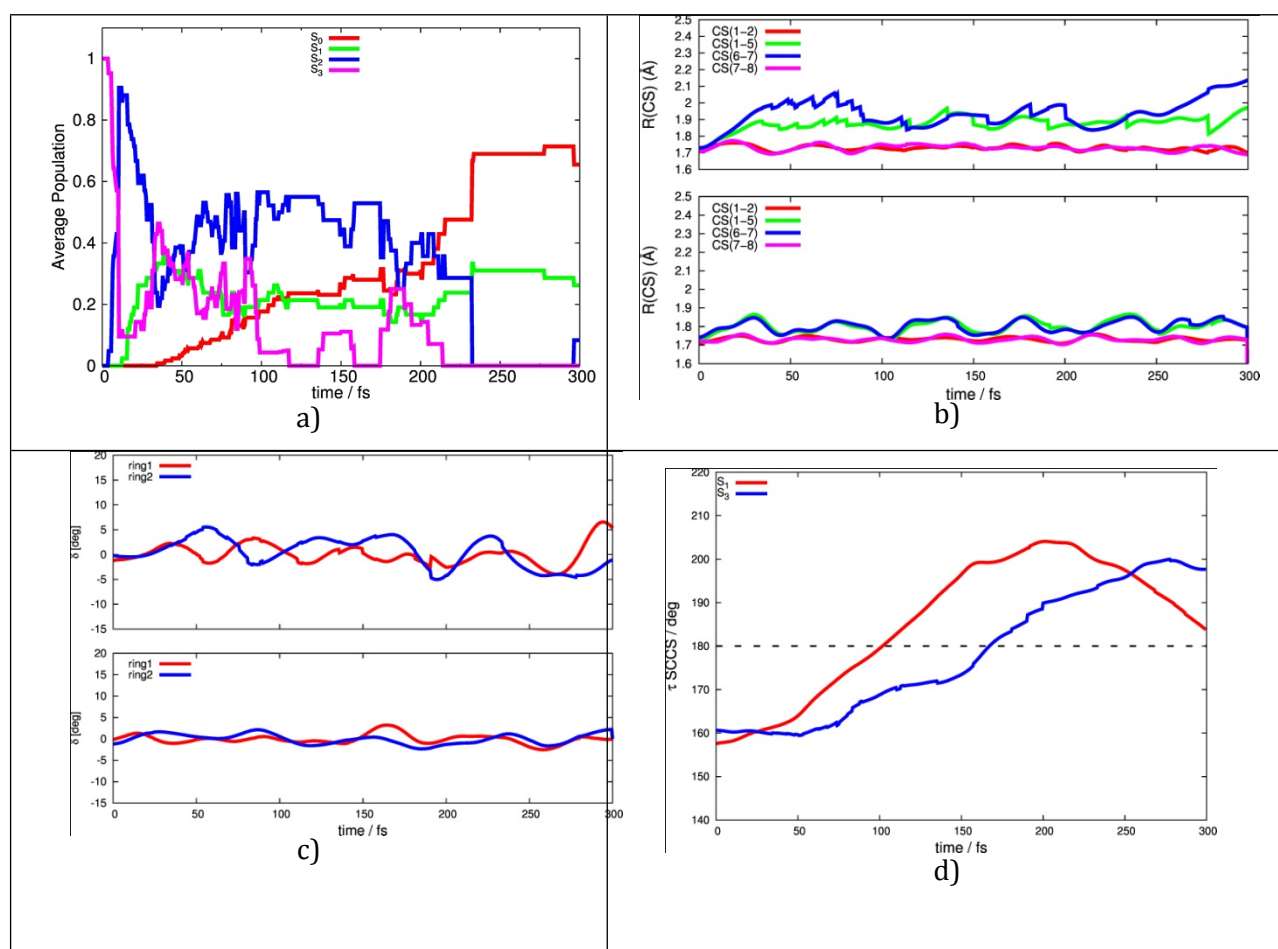
**Figure S10.1:** Time evolution of the excited-state energies for one trajectory (TD- $\omega$ B97XD/6-31G\*) from 2T high-energy excitation. Snapshots of 2T molecular structure along the dynamics ( $t = 0, 34.5, 75$  fs). Black dots give the currently occupied state during the dynamics.

### S11. TDPBE0/ SVP nonadiabatic excited-state dynamics for 2T: high- vs. low-energy excitations.

In this section, we report the nonadiabatic excited-state dynamics for 2T computed at the PBE0/SVP level, considering both low-energy (population of only  $S_1$ ) and high-energy (population of  $S_3$ ) excitation.

By exciting at low energy, 70 trajectories starting from  $S_1$  were created. 2 trajectories reached the  $S_1/S_0$  crossing within 75 fs, 2 within 150 fs, 2 within 225, and 64 were still in the excited states at 300 fs.

By exciting at high energy, 42 trajectories starting from  $S_3$  were created. 13 trajectories reached the  $S_1/S_0$  crossing within 75 fs, 11 within 150 fs, 4 within 225, and 14 were still in the excited states at 300 fs.



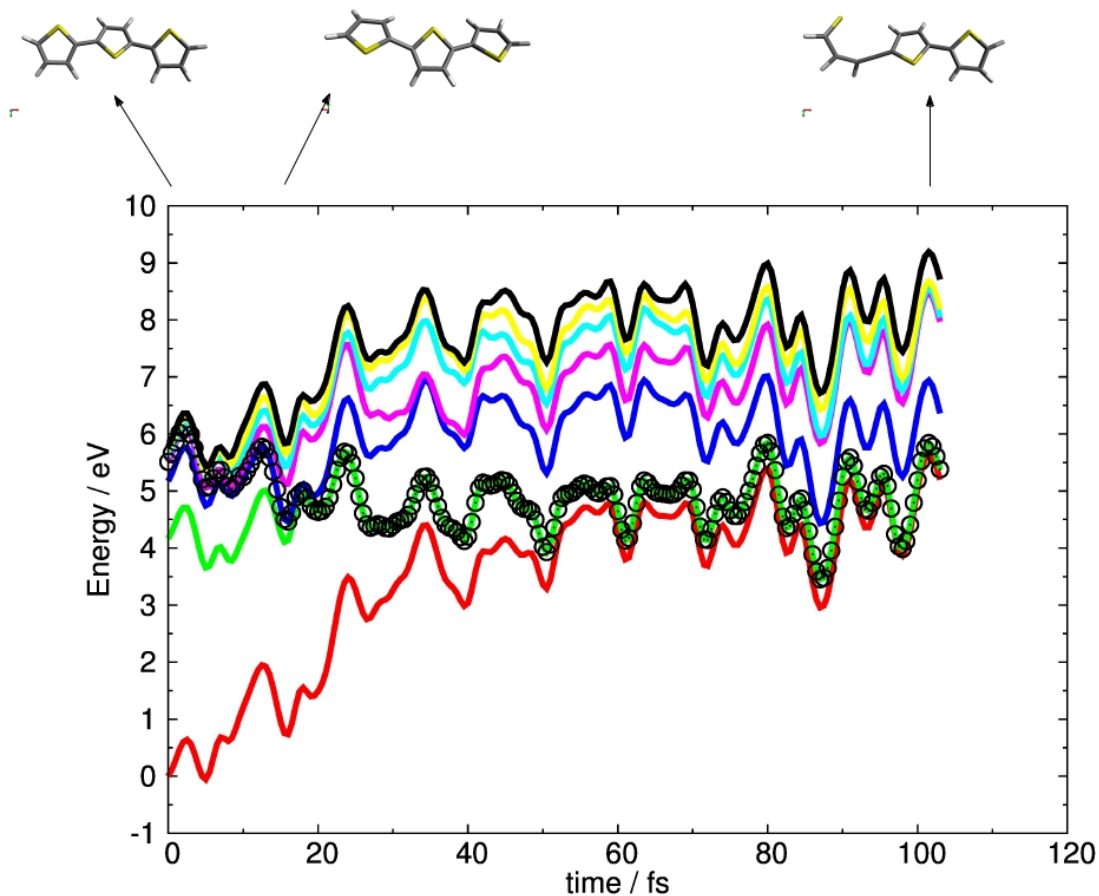
**Figure S9.1:** TDDFT (PBE0)/SVP nonadiabatic excited-state dynamics. Panel a) Evolution of the state population upon high-energy excitation vs. time. Panel b) Upper: C-S bond length variations upon high-energy excitation; Bottom: C-S bond length variations upon low-energy excitation. Panel c) Upper: ring puckering variations upon high-energy excitation; Bottom: ring puckering variations upon low-energy excitation. Panel d) dihedral angle variations upon high-energy (red) and low-energy (blue) excitations.

Similar conclusions, as those reported in the manuscript for  $\omega$ B97XD functional, can be drawn for the case of PBE0/SVP. Upon high-energy excitation, an ultrafast internal conversion ( $\sim 70$  fs) occurs and the photoexcited population is transferred *via* nonadiabatic processes from  $S_3$  to  $S_2$  and  $S_1$ . Within 300 fs, the  $S_0$  occupation reaches 60%.

High-energy excitation induces higher distortions and fluctuations in terms of C-S bond elongation and ring puckering. Similarly as for  $\omega$ B97XT, 2T crosses a flat conformation at  $\sim 100$  fs starting from  $S_1$  and at  $\sim 160$  fs starting from  $S_3$ .



**S12. Example of one TDDFT nonadiabatic excited-state dynamics trajectory from high energy excitation of 3T.**



**Figure S11.1:** Time evolution of the excited-state energies for one trajectory (TD- $\omega$ B97XD/6-31G\*) from 3T high-energy excitation. Snapshots of 3T molecular structure along the dynamics (t = 0, 17.5, 103 fs). Black dots give the currently occupied state during the dynamics.