Unveiling the role of *hot* charge-transfer states in molecular aggregates *via* nonadiabatic dynamics

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Supplementary Note 1

1. Ground state geometry optimizations

Geometry optimizations and vibrational frequency analysis for the bi-thiophene dimer were carried out at the DFT level using the ωB97XD functional and the *ab initio* algebraic diagrammatic construction to second order ADC(2) [*see A. Dreuw, M. Wormit, WIREs Comput. Mol. Sci.,* ***2015****, 5, 82*].

For the DFT calculations (using Gaussian09[1]), three basis sets were used, namely 6-31G*, 6-311+G*, and aug-cc-pVTZ. For ADC(2) (using TURBOMOLE[2]), the SVP and def2-TZVP basis sets were adopted. The dimer geometries were optimized in *vacuum* without any structural constraints. No imaginary frequencies were obtained, i.e. stable equilibrium geometries were found.

Environmental effects were considered *via* the conductor solvent model C-PCM. To simulate the bi-thiophene crystalline mean field, a dielectric constant of 2.25 was chosen. Ground state geometries optimizations with C-PCM were done with the ωB97XD functional using the 6-31G* and 6-311+G* basis sets.

No significant structural changes were observed in the presence of the dielectric compared with the *vacuum* case. There were changes of ±0.01Å in bond lengths and ±2° in bond angles.

1. Gaussian 09, J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009

2. Ahlrichs, R.; Bär, M.; Häser, M; Horn, H.; Kölmel, C *Chem. Phys. Lett.*, **1992**, *97*, 2571-2577.

Cartesian coordinates of the optimized geometries are reported at the end of the Supplementary Information document.

2. Excited states: singlets

Vertical excitation energies were computed *via* TD-DFT and ADC(2) methods.

In Table S1 and Table S2 we report the TDDFT vertical transition energies in the gas phase and in the condensed phase (C-PCM). For the first 14 excited states we list the energy (eV), oscillator strength, and state classification.

Excited states are classified as charge transfer (CT), localized on molecular site A (loc(A)) or B (loc(B)), or delocalized (deloc). The classification is based on the procedure described in the following paper: *K. Sen, et al., J. Chem. Theory Comput.,* ***2013****, 9, 533–542*.

Table S1: TD(ωB97XD) vertical excitation energies (eV), oscillator strengths f, and state classifications of the bi-thiophene dimer, in *vacuum*.

	ωB97XD		
	6-31G*	6-311+G*	aug-cc-pVTZ
S1	4.362, (f = 0.084) loc(A)	4.259, (f = 0.092) loc(A)	4.113, (f = 0.097) loc(A)
S2	4.675, (f = 0.576) loc(B)	4.597, (f = 0.537) loc(B)	4.304, (f = 0.451) loc(B)
S3	5.085, (f = 0.011) deloc	5.030, (f = 0. 011) deloc	4.815, (f = 0.000) Deloc
S4	5.270, (f = 0.015) loc(B)	5.232, (f = 0.014) loc(B)	4.878, (f = 0.001) loc(B)
S5	5.512, (f =0.048) loc(A)	5.397, (f = 0.006) loc(A)	5.266, (f = 0.000) Deloc
S6	5.574, (f = 0.001) deloc	5.452, (f = 0.002) deloc	5.323, (f = 0.002) loc(A)
S7	5.694, (f = 0.013) loc(B)	5.592, (f = 0.010) loc(B)	5.414, (f = 0.045) loc(B)
S8	5.717, (f = 0.135) loc(B)	5.599, (f = 0.096) loc(B)	5.543, (f = 0.131) loc(B)
S9	5.745, (f = 0.002) loc(B)	5.617, (f = 0.038) deloc	5.607, (f = 0.004) Deloc
S10	5.773, (f =0.012) loc(A)	5.650, (f = 0.004) deloc	5.617, (f = 0.004) Deloc
S11	5.880, (f = 0.011) loc(A)	5.803, (f = 0.011) deloc	5.660, (f = 0.001) Deloc
S12	5.993, (f = 0.019) loc(B)	5.855, (f = 0.017) loc(A)	5.743, (f = 0.007) loc(A)
S13	6.039, (f = 0.000) deloc	5.904, (f = 0.019) deloc	5.751, (f = 0.001) Deloc
S14	6.109, (f = 0.009) deloc	5.914, (f = 0.021) deloc	5.775, (f = 0.009) Deloc

Table S2: TD(ωB97XD) vertical excitation energies (eV), oscillator strengths f, and state classifications of the bi-thiophene dimer, in a dielectric *medium*.

	ωB97XD	
	6-31G*	6-311+G*
S1	4.308, (f = 0.208) loc(A)	4.162, (f = 0.207) loc(A)
S2	4.588, (f = 0.699) loc(B)	4.461 (f = 0.686) loc(B)
S3	5.147, (f = 0.012) deloc	5.035 (f = 0.017) Deloc

S4	5.282, (f = 0.019) loc(B)	5.182 (f = 0.020) loc(B)
S5	5.503, (f =0.007) loc(A)	5.340 (f = 0.007) loc(A)
S6	5.570, (f = 0.005) deloc	5.405 (f = 0.005) Deloc
S7	5.685, (f = 0.132) loc(B)	5.539 (f = 0.044) loc(B)
S8	5.691, (f = 0.146) loc(B)	5.546 (f = 0.258) loc(B)
S9	5.753, (f = 0.003) loc(B)	5.613 (f = 0.003) Deloc
S10	5.795, (f =0.001) loc(A)	5.675 (f = 0.000) Deloc
S11	5.902, (f = 0.016) deloc	5.793 (f = 0.004) loc(A)
S12	6.017, (f = 0.025) deloc	5.851 (f = 0.030) Deloc
S13	6.028, (f = 0.000) deloc	5.874 (f = 0.041) Deloc
S14	6.078, (f = 0.013) loc(A)	5.990 (f = 0.007) loc(A)

Environmental dielectric effects do not lead to any significant change in the excited state energies and their character. There are changes of ±0.05eV when going from gas to condensed phase.

In Table S3, we report ADC(2) excitation energies (def-SVP and def2-TZVP basis sets) for the bi-thiophene dimer, computed at the MP2 optimized structure.

Table S3: ADC(2) vertical excitation energies (eV) and oscillator strengths f of the bi-thiophene dimer computed at the optimized MP2 geometry.

	def-SVP	def2-TZVP
S1	4.505 (f = 0.055)	4.204 (f = 0.041)
S2	4.860 (f = 0.717)	4.517 (f = 0.661)
S3	5.082 (f = 0.023)	4.696 (f = 0.068)
S4	5.224 (f = 0.031)	4.820 (f = 0.016)
S5	5.326 (f = 0.032)	5.076 (f = 0.006)
S6	5.408 (f = 0.003)	5.170 (f = 0.000)
S7	5.551 (f = 0.203)	5.276 (f = 0.003)
S8	5.558 (f = 0.007)	5.331 (f = 0.146)
S9	5.877 (f = 0.004)	5.549 (f = 0.002)
S10	5.979 (f = 0.006)	5.657 (f = 0.002)
S11	6.128 (f = 0.000)	5.711 (f = 0.004)
S12	6.264 (f = 0.005)	5.765 (f = 0.012)
S13	6.354 (f = 0.004)	5.854 (f = 0.024)
S14	6.417 (f = 0.004)	5.885 (f = 0.011)

Equilibrium geometries of the low-lying excited states S_1^{AB} and S_2^{AB} were optimized at the TDDFT level. The excited-state relaxation energies, E_{rel} (i.e., the energy difference between the Franck-Condon point and the excited-state minimum) are given in Table S4.

Table S4: TD(ωB97XD) exciton relaxation energy (E_{rel} / eV) for S_1^{AB} and S_2^{AB}.

	6-31G*	6-311+G*
E_{rel} S_1^{AB}	0.904	0.866
E_{rel} S_2^{AB}	0.909	0.917

Cartesian coordinates of all optimized excited-state geometries are reported at the end of the Supporting Information document.

3. Excited states: double excitations and triplets

The effects of double excitations were checked at the DFT/MRCI level [*see S. Grimme, M. Waletzke, J. Chem. Phys.,* ***1999****, 111, 5645*]. In Table S5 we report the DFT/MRCI results for the first nine singlet excited states, i.e. the energies and the contributions from single, double, triple, and quadrupole excitations. The contributions from double excitations are negligible (<10%) in the excited states considered relevant for the ultrafast dynamics here investigated.

Table S5: DFT/MRCI results for singlet excited states for bi-thiophene dimer computed at the optimized (ωB97XD/6-311+G*) ground-state geometry. Relative energies (ΔE in eV) and contributions (%) of single, double, triple, and quadruple excitations to the wave function.

	ΔE	Single	Double	Triple	Quadruple
S0	0	0	3.9	0	0
S1	3.8571	93.4	3.7	2.9	0
S2	4.1128	93.0	3.7	3.2	0
S3	4.4700	87.7	9.8	2.4	0.1
S4	4.6069	86.5	10.6	2.8	0.1
S5	4.6126	85.0	12.2	2.6	0.2
S6	4.7259	87.0	10.1	2.8	0.1
S7	4.8318	85.7	11.3	2.8	0.1
S8	4.8606	85.7	11.3	2.9	0.1
S9	4.9185	75.4	21.5	2.7	0.3

Triplet states were computed at the U-ωB97XD level with the 6-31G*, 6-311+G*, and aug-cc-pVTZ basis sets. The geometry of the T_1 state was optimized, and vertical transitions (T_1 -> T_n) were calculated at each level of theory. Results are reported in Table S6.

Table S6: S_0-T_1 adiabatic excitation energies (eV) and T_1-T_n vertical excitation energies (eV) and oscillator strengths f computed at the TD-ωB97XD level with different basis sets.

	6-31G*	6-311+G*	aug-cc-pVTZ
Δ(S_0-T_1)	2.278	2.249	2.341
T2	4.132 (f = 0.004)	4.105 (f = 0.003)	4.159 (f = 0.003)
T3	4.789 (f = 0.011)	4.642 (f = 0.003)	4.731 (f = 0.013)
T4	4.858 (f = 0.010)	4.708 (f = 0.017)	4.860 (f = 0.007)
T5	4.903 (f = 0.000)	4.728 (f = 0.001)	4.874 (f = 0.001)

T6	4.949 (f = 0.001)	4.808 (f = 0.015)	4.993 (f = 0.000)
T7	5.048 (f = 0.006)	4.992 (f = 0.011)	5.028 (f = 0.006)
T8	5.185 (f = 0.000)	5.108 (f = 0.000)	5.210 (f = 0.000)
T9	5.472 (f = 0.000)	5.675 (f = 0.000)	5.484 (f = 0.000)
T10	5.783 (f = 0.269)	5.856 (f = 0.253)	5.614 (f = 0.223)
T11	6.058 (f = 0.000)	5.934 (f = 0.010)	5.656 (f = 0.005)
T12	6.108 (f = 0.000)	6.049 (f = 0.002)	5.902 (f = 0.001)
T13	6.329 (f = 0.003)	6.138 (f = 0.000)	5.987 (f = 0.000)
T14	6.404 (f = 0.001)	6.179 (f = 0.007)	6.056 (f = 0.000)

4. Absorption spectra

Absorption spectra were generated using the nuclear ensemble method, considering 150 points and 20 excited states. The spectra were computed with the ωB97XD functional, using the 6-31G* and 6-311+G* basis sets, in *vacuum* and with a dielectric environment. The spectra are shown in Figure S1.

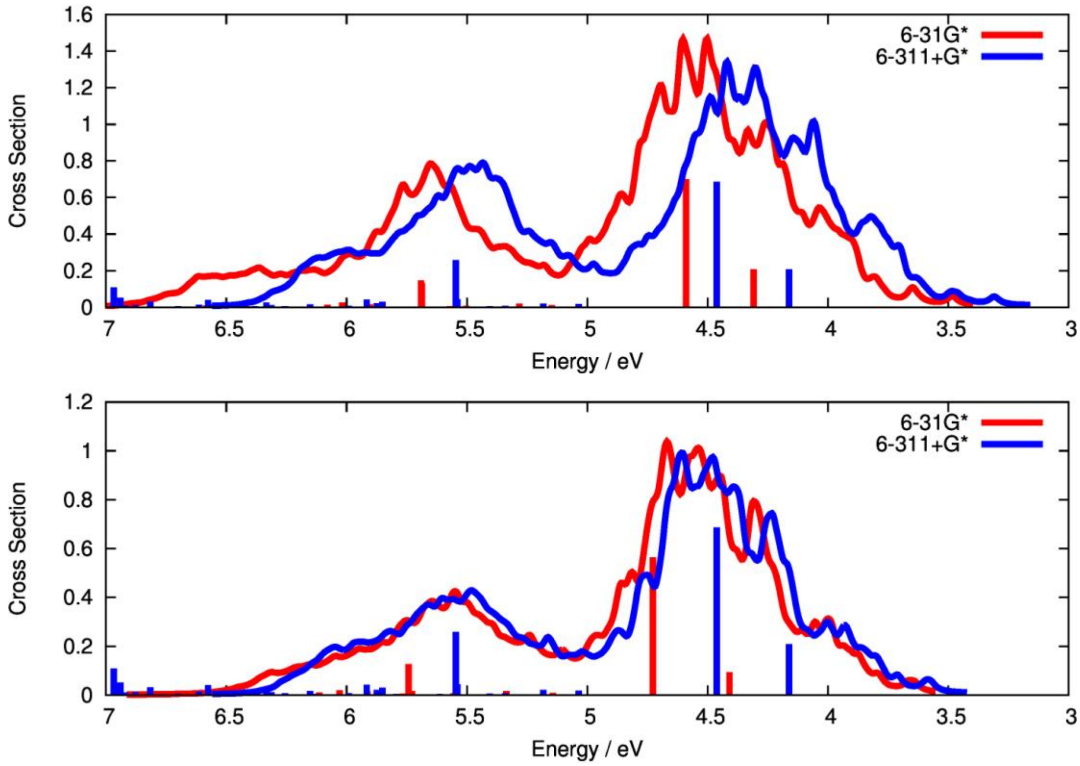


Figure S1: Absorption spectra (Å^2 molecule^{-1}) computed at the TDDFT (ωB97XD) level with different basis sets (6-31G* (red) and 6-311+G* (blue)), in *vacuum* (bottom panel) and in a dielectric environment (upper panel).

Supplementary Note 2

For the nonadiabatic excited state dynamics calculations, overall 30 trajectories have been considered. For each trajectory, 10 electronic states have been taken into account and the integration time step, for updating the nuclear positions and velocities, has been set to 0.5 fs. This leads to 600 quantum chemical calculations (one each time step) to be run to evaluate the electronic energies, the energy gradient and the nonadiabatic coupling terms amongst all the excited states (i.e. nine excited states). Trajectories were computed in parallel on our local HPC cluster; each trajectory ran on a single node (Intel Xeon E5-2690 v2, 3.00 GHz), using 8 CPUs and 800 MW memory for the quantum chemical calculations. Each time step of the surface hopping dynamics required roughly 4 hours, leading to *circa* 100 days to complete one entire (300 fs) trajectory.

1. Fitting procedure for the HE and LE state occupations

The time constant for depopulation of the HE band was obtained by fitting the occupation of this band (sum of occupations from S_3 to S_9) by the exponential function

$$f_e(t) = f_0 + (1 - f_0)\exp\left(\frac{-(t-\tau_L)}{\tau_D}\right), \tag{1}$$

where f_0 is the asymptotic population, τ_L is the latency time before the start of the deactivation, and τ_D is the exponential decay time. The lifetime is given by

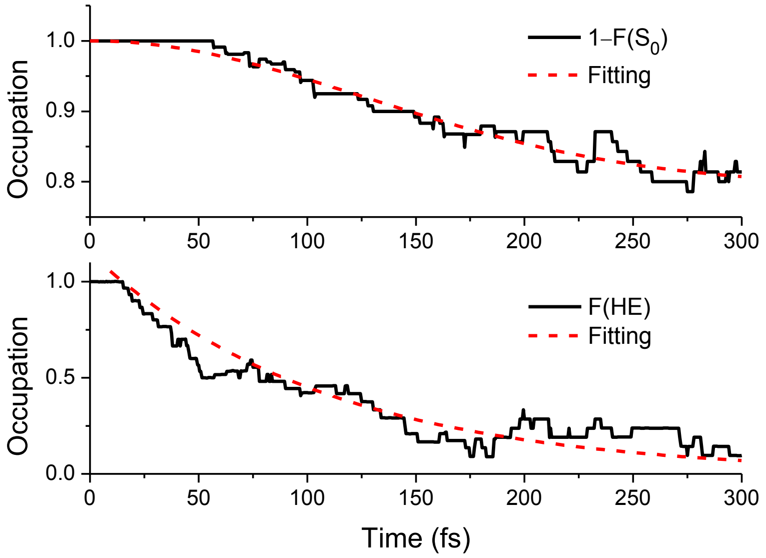
$$\tau = \tau_L + \tau_D\,. \tag{2}$$

The population of the ground state was obtained by fitting the complementary occupation $1-F(S_0)$ with the Gaussian function

$$f_g(t) = f_0 - (1 - f_0)\exp\left(\frac{-t^2}{\pi\tau^2}\right). \tag{3}$$

The factor π is included in the exponential term to guarantee that τ is the average time over the 0-∞ range.

	f_0	τ_L (fs)	τ_D (fs)	τ (fs)
F(HE)	1.0	15	107	122
$1-F(S_0)$	0.8	-	-	102


Occupation
1.0
0.9
0.8
1−F(S_0)
Fitting
0
50
100
150
200
250
300
Occupation
1.0
0.5
0.0
F(HE)
Fitting
0
50
100
150
200
250
300
Time (fs)

Supplementary Note 3

1. Time-dependent oscillations of internal coordinates: ring puckerings, carbon-carbon oscillations and torsional angles

Below we report the time dependent evolution of the ring puckering and the intra-molecular dihedral angle oscillations. Results have been averaged over all 30 computed trajectories.

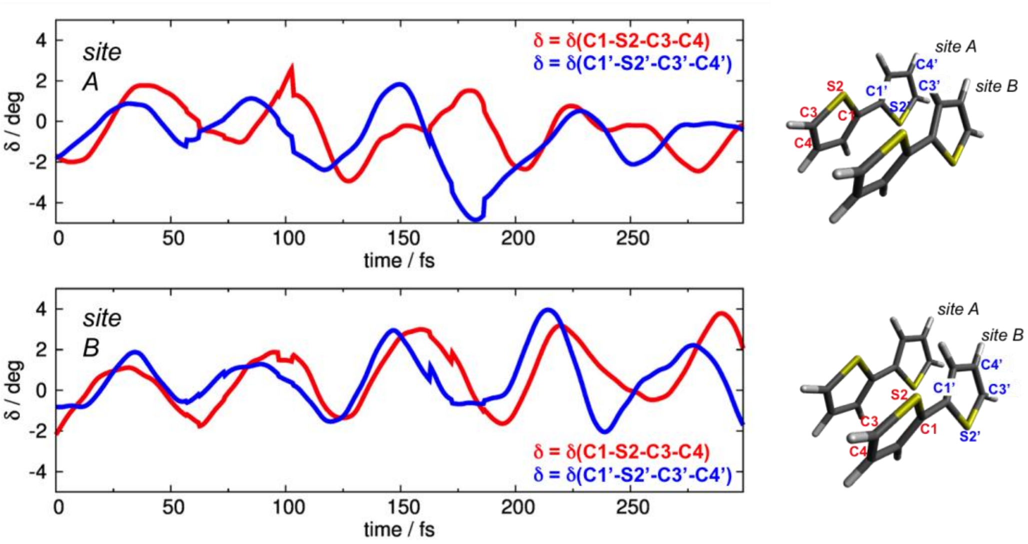


Figure S2: Ring puckering oscillations of the bi-thiophene dimer rings; the top (bottom) panel corresponds to ring puckering on molecular site A (B). The ring puckering is defined as the dihedral angle amongst atoms belonging to the thiophene ring: δ = ∠(C-S-C-C), as sketched in the molecular structures on the right side.

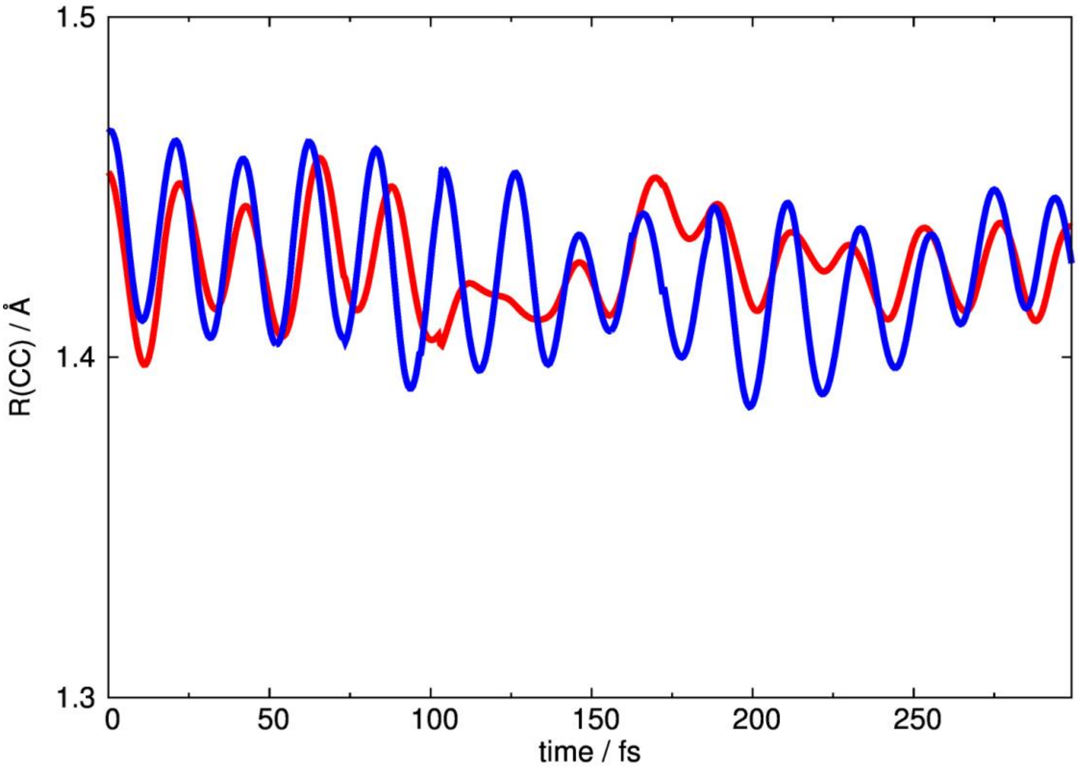


Figure S3: Central carbon-carbon bond (C1-C1', see molecular sketch Figure S2) length oscillations of the bi-thiophene dimer. Red and blue represent the C-C oscillations for monomer A and B respectively.

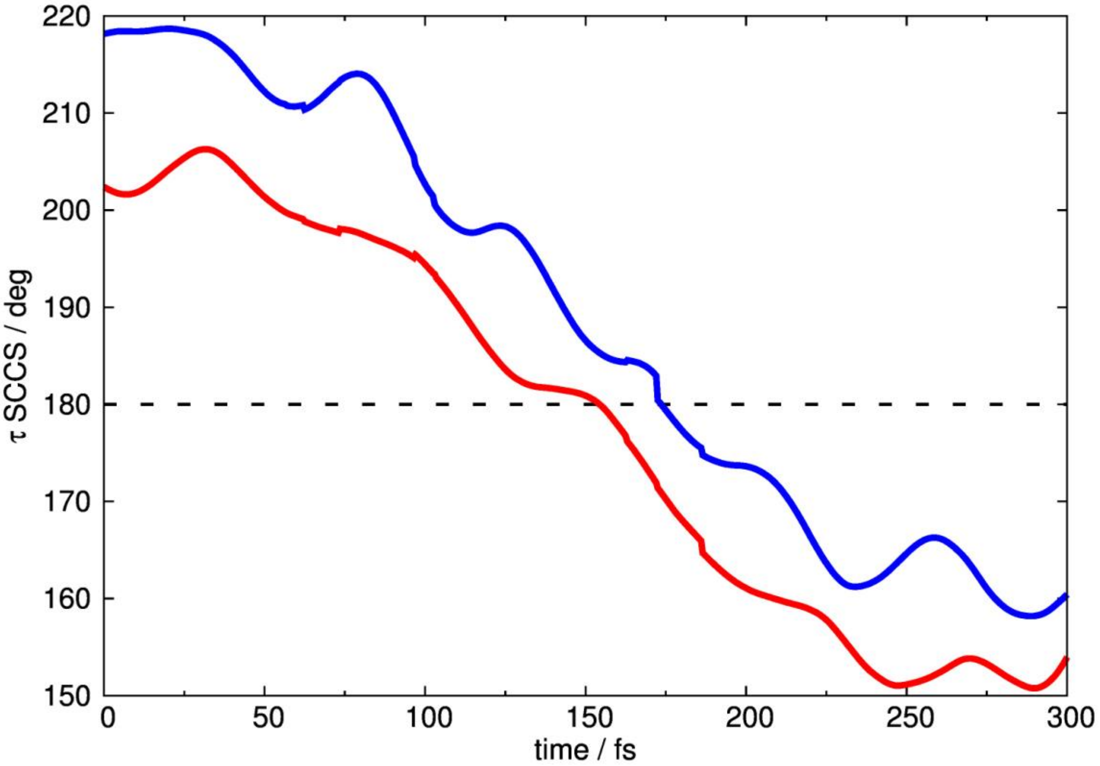


Figure S4: Torsional oscillations of bi-thiophene on molecular site A (red line) and B (blue line) monitored through the intra-molecular angle ∠(S-C-C-S). The dotted black line represents the planar conformation. The dihedral angles on both molecules oscillate with the same phase, passing through the planar conformation within 150 and 175 fs, respectively. The oscillation period is 300 fs.

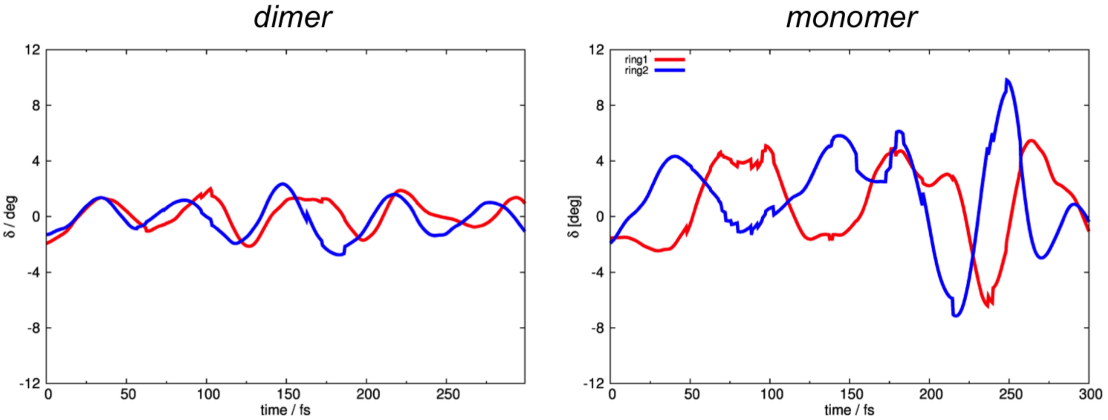
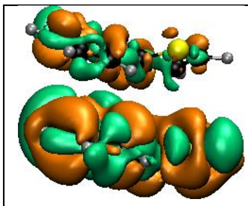
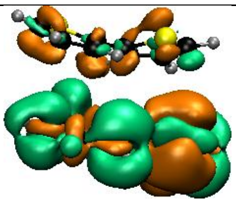
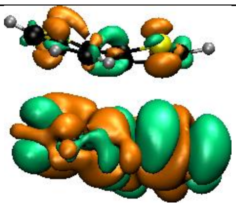
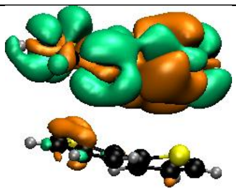
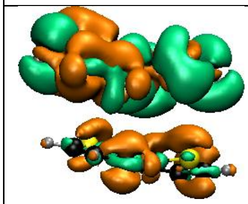
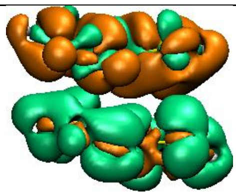
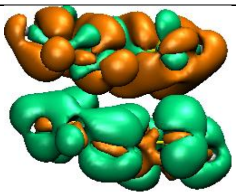
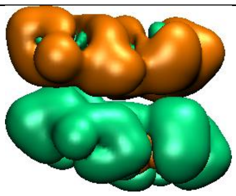
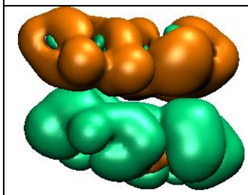
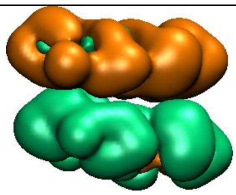
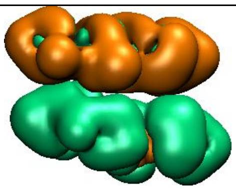
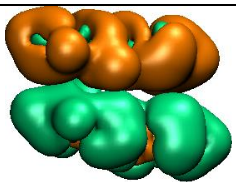
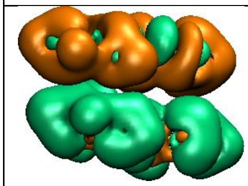
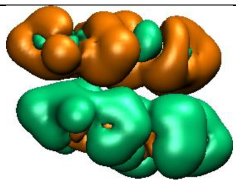
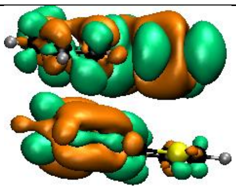
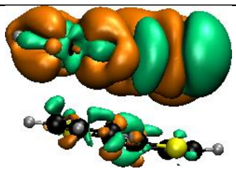
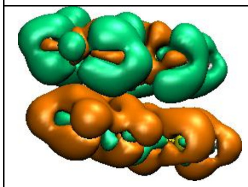
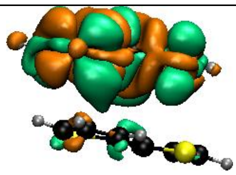
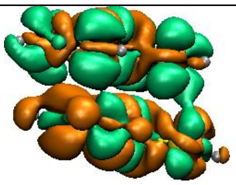
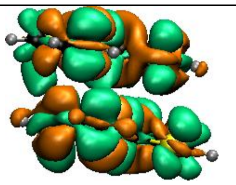
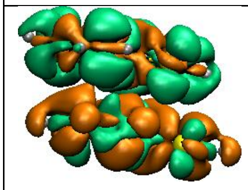
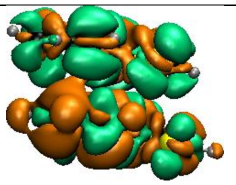
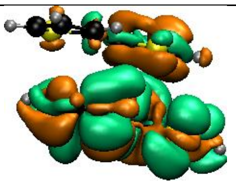
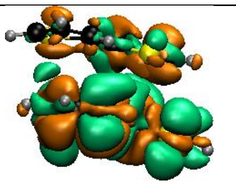


Figure S5: Comparison between the ring puckering oscillations (δ) as evaluated from nonadiabatic excited-state dynamics computed for the bi-thiophene dimer (left side, current work), and from dynamics performed on a single isolated bi-thiophene molecule (right side, *see D. Fazzi et al., Phys. Chem. Chem. Phys., 2015, 17, 7787-7799*). Left side: average δ computed for the molecular site A (blue line) and B (red line). Right side: average δ computed for the first (blue) and second (red) thiophene ring.

2. Nonadiabatic excited state dynamics: electron-hole density for traj A, traj B and the trajectory with frozen Cartesian coordinates for the sulphur and nearest bonded carbon atoms.

Electron-hole densities were mapped during the dynamics. Here we show the results for three exemplary trajectories (traj A, traj B and traj *Frozen* see main article). The electron-hole densities were computed every 10 fs, in each trajectory. In Tables S7, S8 and S9, we present electron-hole density snapshots from traj A, traj B and traj *Frozen*.

Table S7: Electron-hole density computed along traj A every 10 fs.

 t = 0.0 fs	 t = 10.0 fs	 t = 20.0 fs	 t = 30.0 fs
 t = 40.0 fs	 t = 50.0 fs	 t = 60.0 fs	 t = 70.0 fs
 t = 80.0 fs	 t = 90.0 fs	 t = 100.0 fs	 t = 110.0 fs
 t = 120.0 fs	 t = 130.0 fs	 t = 140.0 fs	 t = 150.0 fs
 t = 160.0 fs	 t = 170.0 fs	 t = 180.0 fs	 t = 190.0 fs
 t = 200.0 fs	 t = 210.0 fs	 t = 220.0 fs	 t = 230.0 fs

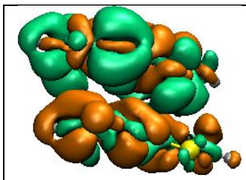
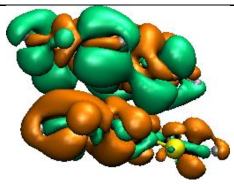
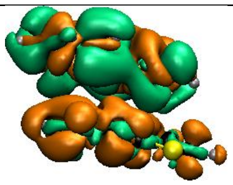
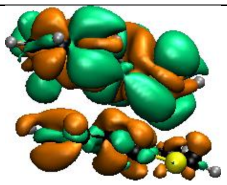
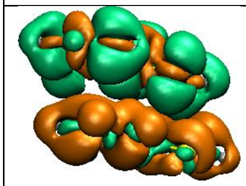
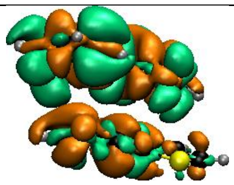
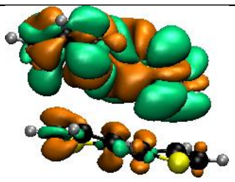
 t = 240.0 fs	 t = 250.0 fs	 t = 260.0 fs	 t = 270.0 fs
 t = 280.0 fs	 t = 290.0 fs	 t = 300.0 fs	

Table S8:Electron-hole density computed along traj B every 10 fs.

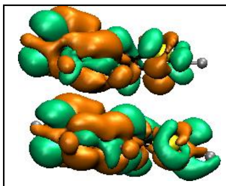
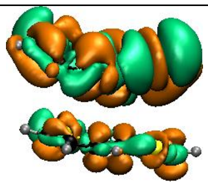
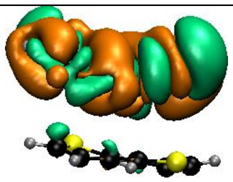
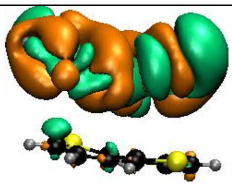
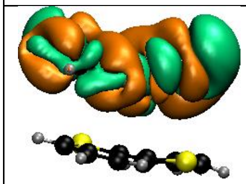
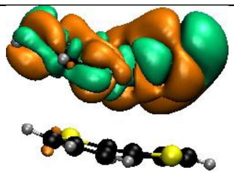
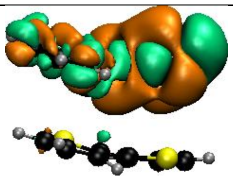
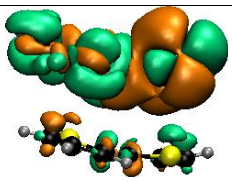
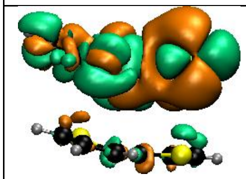
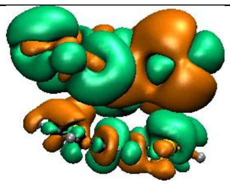
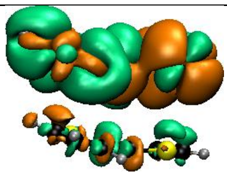
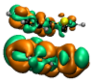
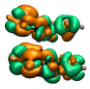
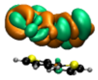
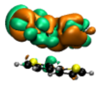
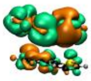
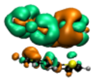
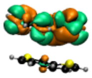
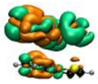
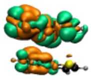
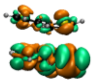
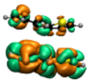
 t = 0.0 fs	 t = 10.0 fs	 t = 20.0 fs	 t = 30.0 fs
 t = 40.0 fs	 t = 50.0 fs	 t = 60.0 fs	 t = 70.0 fs
 t = 80.0 fs	 t = 90.0 fs	 t = 100.0 fs	

Table S9:Electron-hole density computed along traj *frozen* every 10 fs.

 t = 0.0 fs	 t = 10.0 fs	 t = 20.0 fs	 t = 30.0 fs
 t = 40.0 fs	 t = 50.0 fs	 t = 60.0 fs	 t = 70.0 fs
 t = 80.0 fs	 t = 90.0 fs	 t = 100.0 fs	

3. Energies of triplet excited states monitored during the dynamics

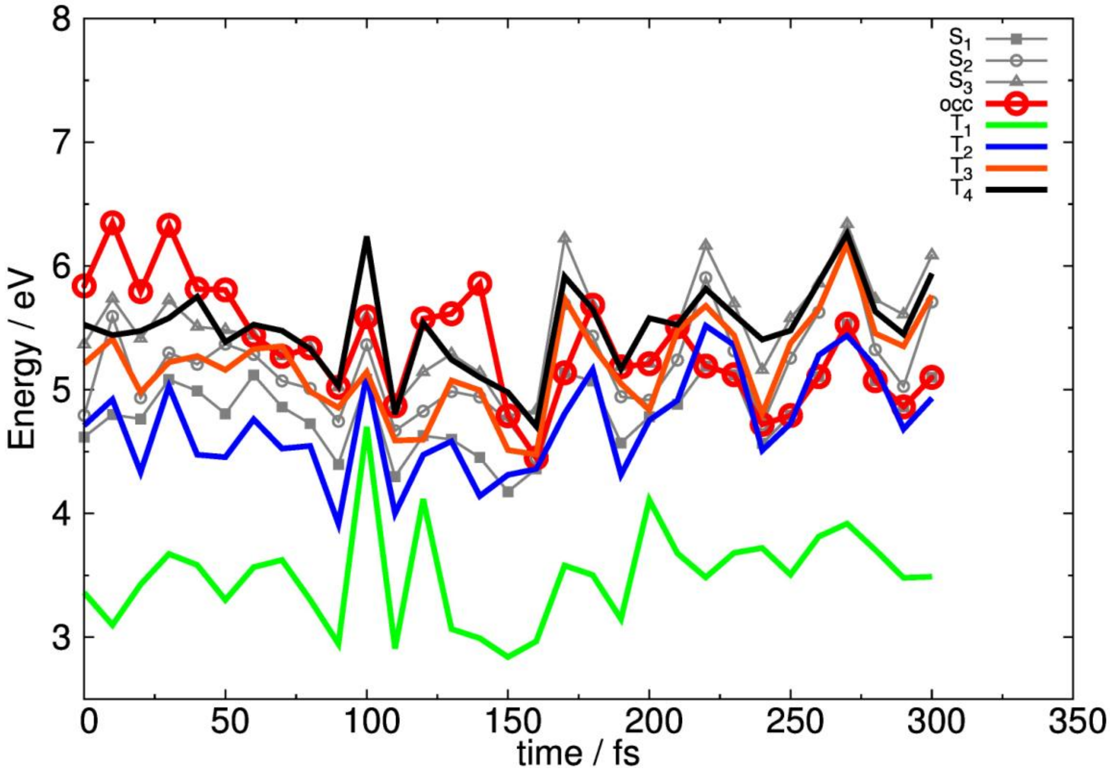
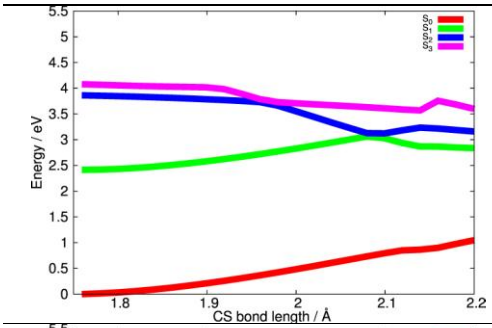


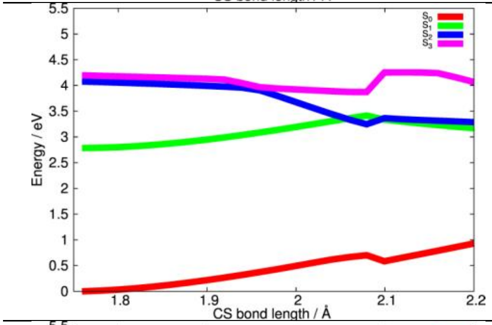
Figure S5: Time-dependent evolution of the energies of the first four triplet states (solid coloured lines) and the first three singlet excited states (grey lines) computed at the TD-ωB97XD/6-31G* level during one trajectory every 10 fs.

4. Relaxed S_1 potential energy profiles: effect of the inter-molecular distance.

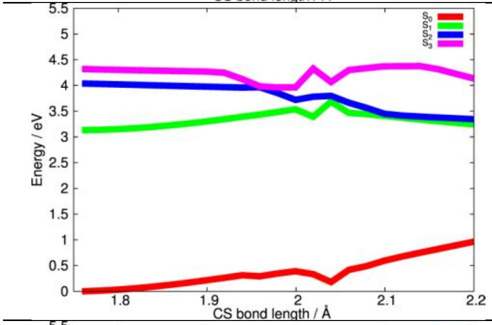
TDDFT (ωB97XD/6-31G*) relaxed (S_1) diabatic potential energy profiles along the C-S stretching coordinate for different values of the inter-molecular distance *d*, namely: 2.5 Å, 4.5 Å and 10.5 Å.



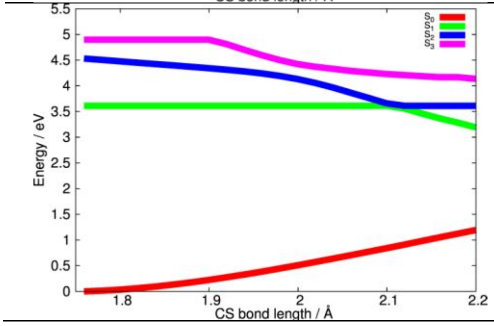
d = 2.5 Å



d (*equilibrium*) ~ 3.5 Å

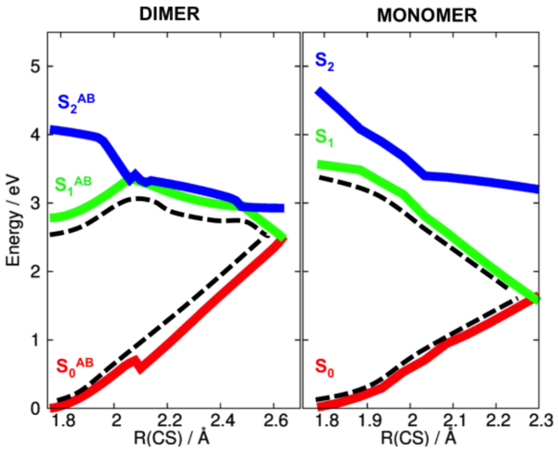


d = 4.5 Å

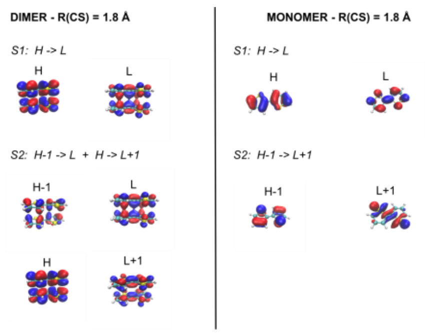


d = 10.5 Å

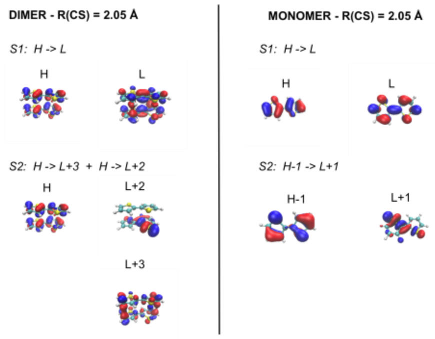
5. Molecular orbital analysis along the C-S potential energy profile: dimer *vs.* monomer.



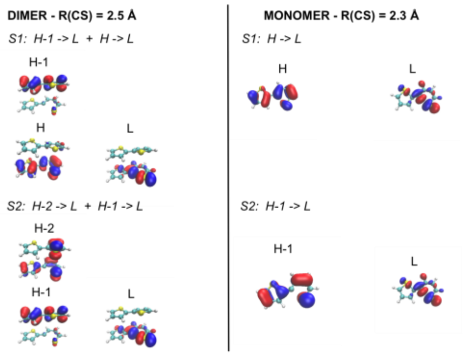
R (C-S) = 1.8 Å



R (C-S) = 2.05 Å



R (C-S) = 2.5 Å (2.3Å for monomer)



Supplementary Note 4

Optimized Cartesian coordinates and total energies

S_0, ωB97XD/6-31G*

(*atom type*, *x y z* coordinates in Å)

C	0.091674	-0.320382	-0.364335
C	0.139089	-0.174897	0.998132
S	1.785210	-0.135242	1.549688
C	2.389320	-0.331455	-0.050718
C	1.379837	-0.407880	-0.963727
C	-0.964016	-0.056225	1.940340
S	-2.527888	0.485941	1.414481
C	-3.181386	0.332717	2.999993
C	-2.244261	-0.099249	3.889939
C	-0.975424	-0.322933	3.284913
H	3.454964	-0.381529	-0.226504
H	1.543459	-0.535721	-2.027282
H	-0.838842	-0.383367	-0.917631
H	-4.214319	0.589587	3.187348
H	-2.446775	-0.255841	4.942789
H	-0.106195	-0.689058	3.820152
C	-0.130088	3.240206	0.365983
C	-0.162751	3.545087	1.700447
S	1.445000	3.795317	2.311821
C	2.142029	3.466676	0.770508
C	1.189990	3.194755	-0.165772
C	-1.318173	3.668663	2.579975
S	-2.799147	4.382697	2.014860
C	-3.564982	4.136023	3.539773
C	-2.721268	3.553777	4.437677
C	-1.435199	3.285040	3.888699
H	3.215669	3.482778	0.643833
H	1.417197	2.944996	-1.194871
H	-1.024726	3.022239	-0.206259
H	-4.592467	4.438740	3.688185
H	-3.004761	3.311494	5.455127
H	-0.634691	2.790471	4.426469

E = -2209.35754693 Hartree

S_1, TD-ωB97XD/6-31G*

C	-0.111118	0.196422	-0.138007
C	-0.139531	0.030232	1.257294
S	1.491011	-0.227334	1.866671
C	2.157607	-0.047683	0.284750
C	1.181902	0.129183	-0.671140
C	-1.246213	0.047013	2.126627
S	-2.891928	0.075288	1.504467
C	-3.541649	0.129396	3.103417
C	-2.558263	0.061267	4.064463
C	-1.262926	0.040619	3.532230
H	3.222764	-0.149321	0.131219
H	1.406326	0.250935	-1.724262
H	-1.007724	0.358113	-0.724607
H	-4.612173	0.145309	3.252975
H	-2.772878	0.073619	5.126592
H	-0.357223	0.013226	4.126519
C	0.096366	3.325505	0.076336
C	0.077627	3.306596	1.481406
S	1.722493	3.270975	2.105489
C	2.374199	3.221536	0.507834
C	1.391904	3.296491	-0.454455
C	-1.029860	3.315817	2.350052
S	-2.658749	3.589463	1.743232
C	-3.325932	3.400772	3.324256
C	-2.352051	3.206197	4.277656
C	-1.059767	3.130866	3.742964
H	3.444815	3.201787	0.359499
H	1.608162	3.288169	-1.516285
H	-0.808700	3.356112	-0.518785
H	-4.390637	3.505784	3.478776
H	-2.577466	3.075459	5.329480
H	-0.164308	2.955611	4.327371

E = -2209.22867321 Hartree

S_2, TD-ωB97XD/6-31G*

C	0.471756	-0.219799	-0.572594
C	0.427265	-0.276412	0.800265
S	1.974508	-0.758014	1.436903
C	2.655691	-0.863719	-0.141307
C	1.743959	-0.553761	-1.107840
C	-0.683824	0.016315	1.678588
S	-2.265201	0.372568	1.036441
C	-2.910308	0.602682	2.611065
C	-1.968531	0.403863	3.584970
C	-0.701266	0.064642	3.054426
H	3.688745	-1.157061	-0.267454
H	1.969537	-0.562471	-2.167606
H	-0.378381	0.073132	-1.178341
H	-3.943465	0.892938	2.739445
H	-2.175324	0.516400	4.641375
H	0.178910	-0.112918	3.661437
C	-0.520388	3.388322	0.497488
C	-0.519649	3.385963	1.924634
S	1.109357	2.988903	2.534641
C	1.691147	2.788737	0.922601
C	0.717361	3.049468	-0.035076
C	-1.561822	3.618550	2.806041
S	-3.180680	4.055109	2.215939
C	-3.797562	4.078290	3.833943
C	-2.825806	3.787742	4.775630
C	-1.569195	3.530259	4.227902
H	2.716202	2.493355	0.747070
H	0.920495	2.971070	-1.096821
H	-1.407835	3.616292	-0.080587
H	-4.833784	4.329863	4.013685
H	-3.035517	3.767615	5.839416
H	-0.680311	3.285501	4.797754

E = -2209.21713143 Hartree

T_1, UωB97XD/6-31G*

C	-0.564802	0.083792	-0.258607
C	-0.251439	-0.039987	1.158863
S	1.516617	-0.178449	1.363192
C	1.752407	-0.081834	-0.357871
C	0.554492	0.052011	-1.061070
C	-1.106560	-0.073489	2.206498
S	-2.877265	0.015101	1.997409
C	-3.116476	-0.123643	3.714917
C	-1.917486	-0.230972	4.420900
C	-0.794271	-0.202331	3.623735
H	2.751005	-0.124957	-0.769508
H	0.523561	0.129417	-2.142138
H	-1.582449	0.192804	-0.613742
H	-4.117216	-0.114682	4.123531
H	-1.888086	-0.325623	5.500641
H	0.225651	-0.266927	3.983187
C	0.518353	3.316215	0.313223
C	0.178203	3.457080	1.632680
S	1.601754	3.639118	2.614709
C	2.634784	3.508813	1.241460
C	1.924067	3.346310	0.090435
C	-1.147616	3.485519	2.230922
S	-2.535316	3.950346	1.292469
C	-3.589049	3.737975	2.639775
C	-2.909040	3.343585	3.752605
C	-1.512066	3.198281	3.519922
H	3.707896	3.555859	1.364554
H	2.381605	3.236959	-0.885460
H	-0.214651	3.164644	-0.470528
H	-4.650570	3.911013	2.529883
H	-3.383678	3.149099	4.706851
H	-0.806283	2.862379	4.270599

E = -2209.27380434 Hartree

S_0, ωB97XD/6-311+G*

C	0.067183	-0.330094	-0.349212
C	0.121843	-0.160527	1.007837
S	1.769019	-0.088364	1.546898
C	2.363460	-0.304311	-0.052630
C	1.350570	-0.409936	-0.955814
C	-0.975530	-0.050778	1.956662
S	-2.536128	0.511634	1.448720
C	-3.184832	0.323971	3.030289
C	-2.249579	-0.134869	3.905387
C	-0.985106	-0.349881	3.292152
H	3.427920	-0.339416	-0.233342
H	1.510050	-0.552527	-2.017313
H	-0.865085	-0.418327	-0.894247
H	-4.215263	0.582152	3.223963
H	-2.451169	-0.314863	4.953898
H	-0.118231	-0.735682	3.815339
C	-0.101415	3.234798	0.364905
C	-0.143055	3.555580	1.693006
S	1.456739	3.842443	2.304138
C	2.161595	3.507719	0.769988
C	1.218312	3.206856	-0.163268
C	-1.302881	3.672524	2.566670
S	-2.770859	4.410340	2.003090
C	-3.550396	4.141309	3.515166
C	-2.720481	3.536038	4.407812
C	-1.434006	3.267422	3.865016
H	3.234419	3.542124	0.647689
H	1.452919	2.948334	-1.187732
H	-0.989035	2.994846	-0.207641
H	-4.576073	4.449417	3.658407
H	-3.015989	3.276945	5.416820
H	-0.642835	2.758547	4.401381

E = -2209.58593163 Hartree

S_0, ωB97XD/6-311+G* C-PCM

C	0.075639	-0.317014	-0.357876
C	0.129748	-0.171496	1.002173
S	1.778249	-0.137810	1.545299
C	2.372651	-0.334211	-0.057887
C	1.359333	-0.407689	-0.963828
C	-0.968143	-0.059056	1.950587
S	-2.537133	0.476604	1.435570
C	-3.183237	0.301802	3.020878
C	-2.241220	-0.131649	3.901812
C	-0.973891	-0.339149	3.290595
H	3.437074	-0.382258	-0.236083
H	1.517978	-0.532351	-2.027666
H	-0.855527	-0.375476	-0.908877
H	-4.217655	0.547487	3.210398
H	-2.438964	-0.298015	4.953251
H	-0.102337	-0.702979	3.821800
C	-0.111760	3.232035	0.368811
C	-0.152480	3.549300	1.697771
S	1.449936	3.829428	2.309183
C	2.153829	3.498715	0.772544
C	1.208444	3.202472	-0.160234
C	-1.311345	3.672998	2.572061
S	-2.781441	4.404922	2.002915
C	-3.556891	4.158663	3.521900
C	-2.724810	3.563351	4.419423
C	-1.439681	3.285378	3.876180
H	3.226939	3.529657	0.651322
H	1.441405	2.947049	-1.185934
H	-0.999334	2.995202	-0.205199
H	-4.582829	4.467487	3.661762
H	-3.017945	3.316665	5.432214
H	-0.648525	2.783362	4.419173

E = -2209.59079222 Hartree

S_1, TD-ωB97XD/6-311+G*

C	-0.105478	0.189793	-0.134675
C	-0.134192	0.027176	1.259049
S	1.495180	-0.225275	1.870237
C	2.160109	-0.043114	0.290428
C	1.186019	0.131429	-0.665695
C	-1.240900	0.034129	2.125835
S	-2.883770	0.059425	1.501175
C	-3.535157	0.081852	3.097034
C	-2.554483	0.017822	4.058586
C	-1.260042	0.007070	3.528343
H	3.225402	-0.138624	0.139447
H	1.411685	0.253888	-1.717510
H	-1.000570	0.343643	-0.724086
H	-4.605500	0.090454	3.242708
H	-2.772146	0.014440	5.119242
H	-0.357315	-0.024252	4.125415
C	0.089505	3.333938	0.077230
C	0.071030	3.311690	1.480374
S	1.714762	3.279246	2.104208
C	2.363600	3.229953	0.507882
C	1.382195	3.303600	-0.453645
C	-1.034396	3.325941	2.348974
S	-2.662652	3.592817	1.742381
C	-3.324324	3.432606	3.325761
C	-2.351038	3.241635	4.277954
C	-1.061285	3.162342	3.741907
H	3.433568	3.210229	0.360740
H	1.598824	3.296144	-1.514471
H	-0.813314	3.370900	-0.519380
H	-4.388231	3.539622	3.478919
H	-2.574607	3.125107	5.330910
H	-0.166397	2.997797	4.328758

E = -2209.46124924 Hartree

S_2, TD-ωB97XD/6-311+G*

C	0.470472	-0.218458	-0.560113
C	0.431988	-0.275674	0.810419
S	1.982488	-0.752006	1.440071
C	2.658416	-0.844719	-0.140008
C	1.741814	-0.540387	-1.100747
C	-0.677286	0.007746	1.693660
S	-2.263798	0.342428	1.055648
C	-2.903734	0.576487	2.630667
C	-1.958111	0.391668	3.599965
C	-0.690679	0.062167	3.066854
H	3.692437	-1.129999	-0.268610
H	1.964406	-0.545254	-2.160391
H	-0.383303	0.067853	-1.162236
H	-3.940521	0.850272	2.758199
H	-2.163002	0.504028	4.656127
H	0.191331	-0.104053	3.672845
C	-0.530288	3.367819	0.485973
C	-0.531752	3.373507	1.911055
S	1.098146	3.005658	2.528324
C	1.681651	2.797918	0.922726
C	0.710118	3.040078	-0.040390
C	-1.572671	3.608913	2.788530
S	-3.189954	4.038825	2.200043
C	-3.795621	4.083506	3.817784
C	-2.820920	3.812095	4.760055
C	-1.569006	3.549138	4.209900
H	2.708246	2.506367	0.753802
H	0.917063	2.954752	-1.099707
H	-1.417214	3.578528	-0.097795
H	-4.831044	4.335673	3.997241
H	-3.025752	3.810182	5.823835
H	-0.677839	3.318367	4.780306

E = -2209.45070918 Hartree

T_1, UωB97XD/6-311+G*

C	0.398787	-0.285081	-0.603024
C	0.376408	-0.275153	0.847905
S	2.015491	-0.619245	1.464887
C	2.634320	-0.724381	-0.155644
C	1.651575	-0.529198	-1.121635
C	-0.672522	-0.050425	1.668908
S	-2.319960	0.246424	1.046157
C	-2.922154	0.456636	2.664520
C	-1.933846	0.283021	3.634485
C	-0.692128	-0.003282	3.124832
H	3.680102	-0.940347	-0.318937
H	1.866968	-0.570288	-2.182640
H	-0.490369	-0.102640	-1.192508
H	-3.959026	0.711498	2.825666
H	-2.143833	0.387694	4.691625
H	0.201980	-0.154338	3.715326
C	-0.460062	3.303591	0.537943
C	-0.452914	3.425100	1.900736
S	1.155657	3.204205	2.521621
C	1.788313	2.935106	0.944754
C	0.821118	3.022087	-0.007807
C	-1.569208	3.674358	2.797706
S	-3.129236	4.123986	2.178996
C	-3.812734	4.154156	3.759679
C	-2.889142	3.849325	4.711718
C	-1.607465	3.576134	4.161949
H	2.836700	2.711259	0.815168
H	1.009772	2.869874	-1.062451
H	-1.362099	3.378721	-0.056933
H	-4.854591	4.406707	3.893049
H	-3.111345	3.817986	5.771123
H	-0.748476	3.289932	4.756857

E = -2209.50326477 Hartree

S_0, ωB97XD/aug-cc-pVTZ

C	-0.876157	0.274376	-0.197314
C	-0.354164	-0.032991	1.027022
S	1.337971	-0.356263	0.899484
C	1.332097	-0.058532	-0.787108
C	0.088972	0.259333	-1.234095
C	-1.027587	-0.093973	2.310432
S	-2.745293	-0.251719	2.402542
C	-2.720829	-0.209287	4.114406
C	-1.454682	-0.093500	4.593474
C	-0.485518	-0.026708	3.562509
H	2.244858	-0.138406	-1.352465
H	-0.132074	0.479068	-2.267489
H	-1.915519	0.527809	-0.344767
H	-3.641169	-0.275949	4.669084
H	-1.219822	-0.049385	5.646096
H	0.573045	0.097606	3.736182
C	0.789437	3.347305	0.516461
C	0.222254	3.324937	1.757847
S	1.448050	3.221021	2.975002
C	2.701455	3.209196	1.803925
C	2.203766	3.281726	0.543298
C	-1.183275	3.379955	2.113782
S	-2.400798	3.605753	0.905127
C	-3.658214	3.563041	2.071015
C	-3.167773	3.385332	3.324005
C	-1.755823	3.279687	3.348881
H	3.730369	3.141991	2.113436
H	2.821219	3.280306	-0.341834
H	0.211515	3.390836	-0.394641
H	-4.684626	3.669039	1.764058
H	-3.789512	3.323896	4.203961
H	-1.186094	3.117922	4.251722

E = -2209.71267851 Hartree

T_1, ωB97XD/aug-cc-pVTZ

C	-0.607571	0.070237	-0.246932
C	-0.258094	-0.057092	1.155254
S	1.506215	-0.201386	1.310006
C	1.696518	-0.105097	-0.406734
C	0.484460	0.036135	-1.074565
C	-1.079983	-0.087788	2.222062
S	-2.847226	0.006121	2.062064
C	-3.041660	-0.133035	3.775059
C	-1.828324	-0.242355	4.446311
C	-0.731670	-0.216819	3.624060
H	2.678821	-0.153611	-0.844448
H	0.424628	0.116806	-2.149826
H	-1.629695	0.184537	-0.573521
H	-4.026593	-0.121669	4.209394
H	-1.770080	-0.337389	5.520500
H	0.292994	-0.285226	3.955520
C	0.543120	3.340110	0.333162
C	0.172927	3.453002	1.642310
S	1.568981	3.585027	2.654630
C	2.629798	3.478778	1.312689
C	1.947280	3.355663	0.145500
C	-1.163127	3.491482	2.207190
S	-2.526199	3.914150	1.230806
C	-3.604957	3.748046	2.552482
C	-2.950363	3.394987	3.688398
C	-1.555238	3.246454	3.491720
H	3.695484	3.507744	1.462962
H	2.426017	3.266653	-0.817442
H	-0.170650	3.225709	-0.468894
H	-4.659385	3.914669	2.413212
H	-3.443701	3.234452	4.634607
H	-0.866645	2.944129	4.266500

E = -2209.62662109 Hartree

S_0, ADC(2)/SVP

C	0.6387443	-1.9290697	-2.1493845
C	0.6933923	-1.6902616	-0.7793744
S	2.3318824	-1.5425431	-0.2521585
C	2.9410888	-1.8177867	-1.8292687
C	1.9198623	-1.9909474	-2.7476272
C	-0.3964847	-1.5793311	0.1679453
S	-1.9425564	-0.9911944	-0.3296644
C	-2.6167296	-1.2222572	1.2281336
C	-1.6796203	-1.7147296	2.1192089
C	-0.4171430	-1.9259759	1.5163359
H	4.0196680	-1.8313289	-2.0089060
H	2.0969718	-2.1797222	-3.8114491
H	-0.3064862	-2.0761099	-2.6827428
H	-3.6607290	-0.9610817	1.4190044
H	-1.9074380	-1.9294266	3.1682798
H	0.4561865	-2.3445856	2.0282970
C	0.4901721	1.4134852	-1.4748338
C	0.4512957	1.7252460	-0.1197997
S	2.0434408	2.0325987	0.4817176
C	2.7552062	1.7284094	-1.0474278
C	1.8027240	1.4206066	-2.0029761
C	-0.7021991	1.8501789	0.7489616
S	-2.1503351	2.6082191	0.1806549
C	-2.9434374	2.3757354	1.6836641
C	-2.1148409	1.7656937	2.6085800
C	-0.8394817	1.4589790	2.0752279
H	3.8401880	1.7850947	-1.1718693
H	2.0512975	1.1871558	-3.0425170
H	-0.4122335	1.1793971	-2.0489603
H	-3.9744338	2.7136111	1.8216615
H	-2.4298438	1.5309587	3.6305052
H	-0.0381282	0.9509820	2.6207818

E = -2201.901914785 Hartree

S_0, ADC(2)/def2-TZVP

C	0.6342316	-1.8729398	-2.1862988
C	0.7270510	-1.7118513	-0.8111854
S	2.3669352	-1.6956920	-0.3213737
C	2.9319265	-1.9173096	-1.9088893
C	1.8889281	-1.9862584	-2.8086272
C	-0.3346697	-1.5907424	0.1563599
S	-1.8905487	-1.0554695	-0.3126676
C	-2.5236335	-1.2440471	1.2536847
C	-1.5596881	-1.6909977	2.1323966
C	-0.3142889	-1.8880707	1.5121677
H	3.9909611	-1.9898730	-2.1055434
H	2.0333380	-2.1277952	-3.8713728
H	-0.3163541	-1.9325864	-2.7014118
H	-3.5559504	-1.0021730	1.4555573
H	-1.7556318	-1.8721460	3.1808109
H	0.5696053	-2.2652787	2.0114017
C	0.4724429	1.4586349	-1.4439785
C	0.4094850	1.7153108	-0.0831107
S	1.9838719	1.9027169	0.5660704
C	2.7252660	1.6279776	-0.9400540
C	1.7908225	1.4088255	-1.9294792
C	-0.7555115	1.8613885	0.7544161
S	-2.1985642	2.5490617	0.1362034
C	-3.0091863	2.3842701	1.6237026
C	-2.1879693	1.8373153	2.5857890
C	-0.9057254	1.5367459	2.0927764
H	3.8013343	1.6324955	-1.0275486
H	2.0555831	1.2046916	-2.9578527
H	-0.4137353	1.2960110	-2.0448581
H	-4.0364908	2.7010979	1.7235371
H	-2.5100054	1.6527222	3.6019326
H	-0.1138291	1.0739653	2.6674453

E = -2203.169748472 Hartree