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

Supplement: Optical spectrum, perceived color, refractive index, and non-adiabatic dynamics of the photochromic diarylethene CMTE

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(Dated: December 28, 2013)

I. SUPPLEMENT

A. Spectra of open and closed ring forms

As discussed in the main article, the spectra of the open ring form was calculated as average of two conformers. For one conformer the thiophene rings are oriented approximately antiparallel to each other and for the other one they are oriented approximately parallel. Similar trends for basis set convergence and influence of solvent are found among all DFT-based methods, therefore only the corresponding spectra calculated with TDDFT are shown here. For all DFT calculations PBE0 was used as functional. The RI-CC2 and TDDFT calculations with def2-SVP basis set were done using Turbomole,[1] the other calculations shown in this section using Gaussian 09.[2]

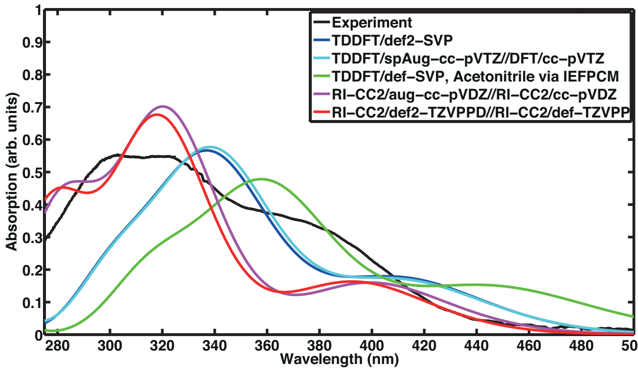

FIG. S1: Absorption spectrum of the antiparallel conformer of the open ring form of CMTE. Computed spectra are shown for different theoretical methods. All spectra are normalized to the respective maximum of the closed ring isomer.

For the antiparallel conformer, the absorption at about 410 nm is similar for all methods shown, see FIG. S1. However, the absorption at about 320 nm is red-shifted compared to the results of the wavefunction-based method. Furthermore, the high-energy shoulder of the absorption is more pronounced with the latter method.

For the parallel conformer, the absorption at 370 nm is more distinct for the RI-CC2 results than for the TDDFT one, see FIG. S2. Furthermore, the absorption is again more pronounced in the low wavelength region with the former method.

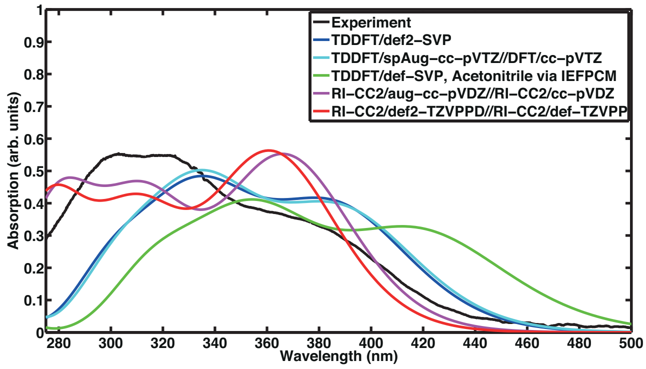

FIG. S2: Absorption spectrum of the parallel conformer of the open ring form of CMTE. Computed spectra are shown for different theoretical methods. All spectra are normalized to the respective maximum of the closed ring isomer.

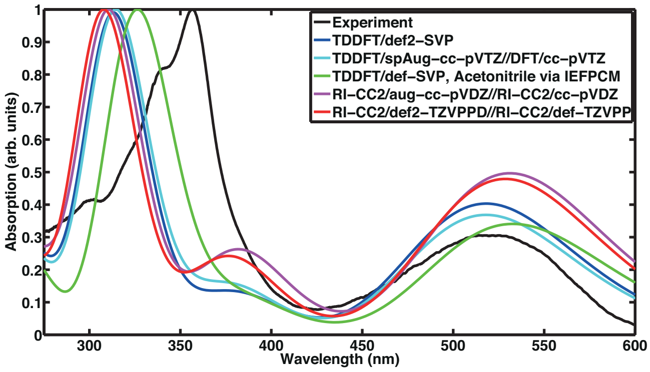

FIG. S3: Absorption spectrum of the closed ring form. Shown are the spectra calculated with different theoretical methods. All spectra are normalized to the respective maximum value.

The absorption of the closed ring isomer is similar for both methods, see FIG. S3. Especially the peaks with higher absorption are quite similar. There is only a slight deviation in the shape of the absorption between the two peaks.

Overall, it can be seen that the inclusion of solvent effects leads to small red-shifts of the absorption. However the quality of the absorption spectra is in general not improved. Furthermore, the results for the DFT-based method seem to be nearly converged, even for the smaller def2-SVP basis set. For the wavefunction-based method the spectrum calculated with aug-cc-pVDZ seems to already yield reliable results, that do not change much, if a larger basis set is used.

B. Estimation of perceived color

Following the description for the estimation of perceived color, the results are first given in CIE tristimulus values. These values can be transformed in different color spaces. The values for two color spaces are therefore given in TABLE S1.

C. Dielectric function and refractive index

For the determination of the static polarizability with PBE0 and RI-MP2, first the structures were optimized using the cc-pVDZ and cc-pVTZ basis sets.[4,5] For the RI-MP2 calculations the corresponding auxiliary basis sets[6] were used. For the calculations of the static polarizability, the augmented versions of the previously mentioned basis sets were used. RI-MP2 is used as a reference for the DFT calculation.[7] The calculations described in this section were done using Turbomole.[1] The static polarizabilities are tabulated in TABLE S2. Both methods show that the polarizability of parallel and antiparallel conformer is similar and that the closed ring form is the structure with the highest polarizability.

D. Reaction mechanism and non-adiabatic ab initio molecular dynamics

In the main article only the trajectories for two categories are shown. The remaining trajectories can be found in FIG. S4 and FIG. S5. Furthermore, animations for trajectories of all four categories can be found online.

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[1] *TURBOMOLE V6.5 2013, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007, available from* `http://www.turbomole.com`.

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TABLE S1: Tabulated values for the perceived colors of open and closed ring isomers as determined from the absorption spectra for daylight conditions. The last column shows the distance between the coordinates of ($L^*a^*b^*$)-values based on calculated absorption spectra to the ($L^*a^*b^*$)-values calculated from the corresponding measured absorption spectrum. This difference is proportional to the deviation in color perception.[3]

	X	Y	Z	x	y	L^*	a^*	b^*	**ΔE**
Open									
Exp.	88.09	93.71	91.12	0.3228	0.3433	97.51	-1.78	7.23	
CC2	93.36	99.84	100.40	0.3180	0.3401	99.94	-2.70	5.23	3.28
TDDFT	90.46	99.33	85.28	0.3289	0.3611	99.74	-7.05	15.19	9.80
TDA	91.76	99.60	92.14	0.3237	0.3513	99.85	-5.15	10.55	5.27
sTDA	88.29	98.16	73.44	0.3397	0.3777	99.29	-9.05	23.36	17.78
Closed									
Exp.	67.69	46.67	61.78	0.3843	0.2650	73.98	58.68	-10.45	
CC2	51.84	28.15	76.35	0.3316	0.1800	60.02	80.84	-46.62	44.66
TDDFT	58.44	34.45	68.44	0.3623	0.2135	65.32	74.67	-31.12	27.54
TDA	73.46	63.71	33.63	0.4301	0.3730	83.82	28.62	36.90	56.93
sTDA	61.05	38.08	61.74	0.3795	0.2367	68.08	68.99	-20.58	15.61

TABLE S2: Static polarizabilities calculated for the three stable structures of CMTE. Further information about the methodology are given in the text.

	PBE0/pVDZ	**PBE0/pVTZ**	**RI-MP2/pVDZ**	**RI-MP2/pVTZ**
Closed	282.30	278.56	278.25	272.99
Parallel	272.47	269.05	266.81	261.98
Antiparallel	271.70	268.37	266.37	261.62

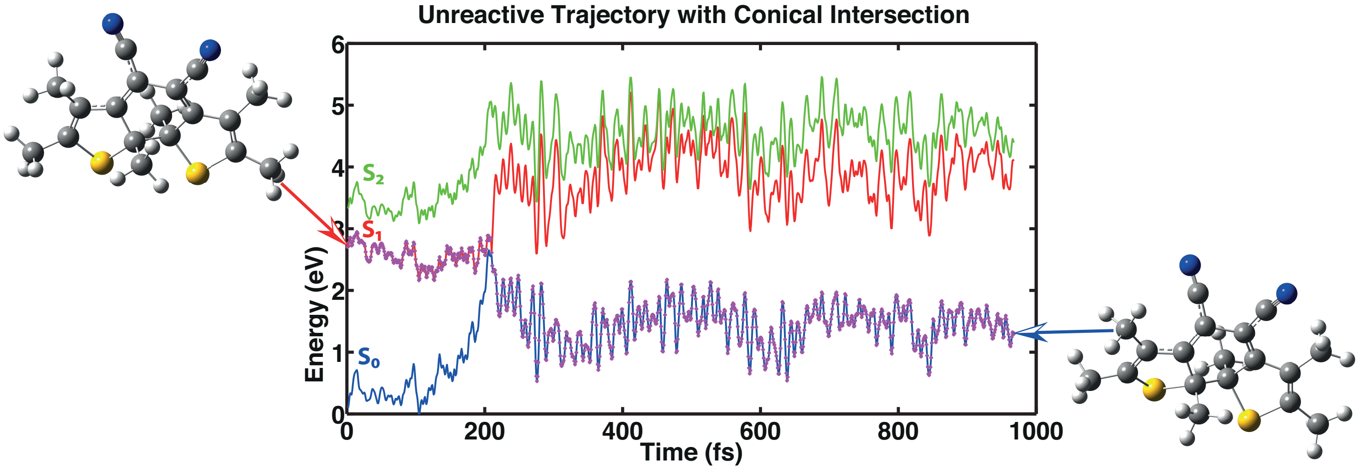

FIG. S4: Example showing an unsuccessful cycloreversion reaction after the trajectory reached the Conical Intersection. The trajectory shown is representative for 9 of the computed 100 trajectories.

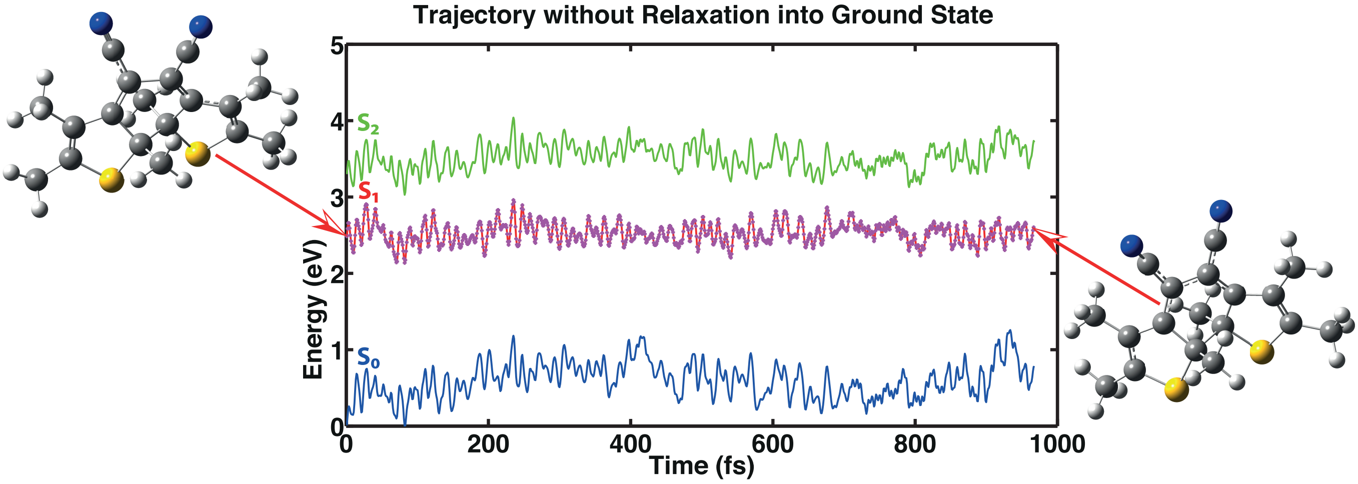

FIG. S5: Example showing one out of 53 trajectories for which the molecule is trapped in the first excited singlet state and does not reach the conical intersection.