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Supporting Information

The Role of Intramolecular Charge Transfer and Symmetry Breaking in the Photophysics of Pyrrolo[3,2-*b*]pyrrole-dione

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1. Absorption and emission spectroscopy

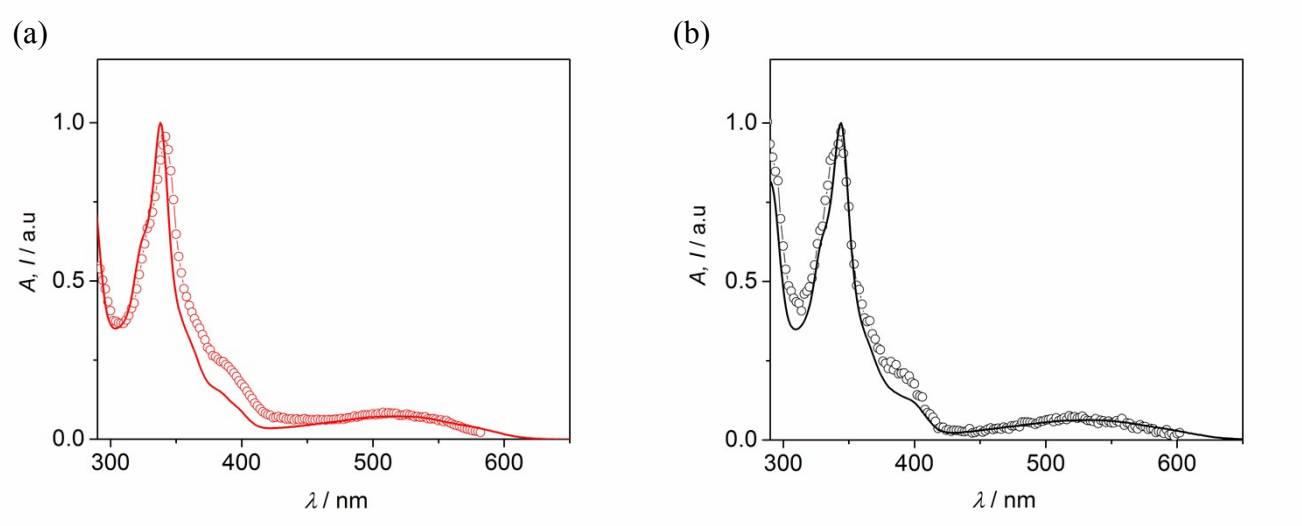


Figure S1: Excitation spectra (circles) and normalized absorption spectra (full lines) of **4** in (a) THF and (b) DCM. Emission collected at 650 nm and 670 nm for THF and DCM, respectively.

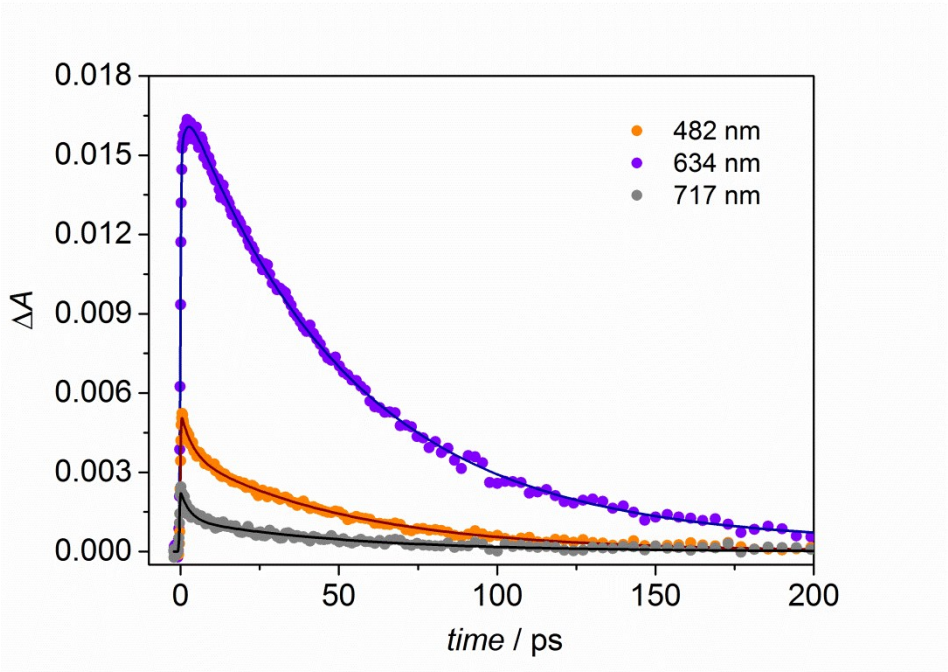


Figure S2: Transient absorption profiles at the indicated wavelengths of a THF solution of **4** upon excitation at 350 nm (A_{350} = 0.2, 0.2 cm optical path). The fittings are reported as lines.

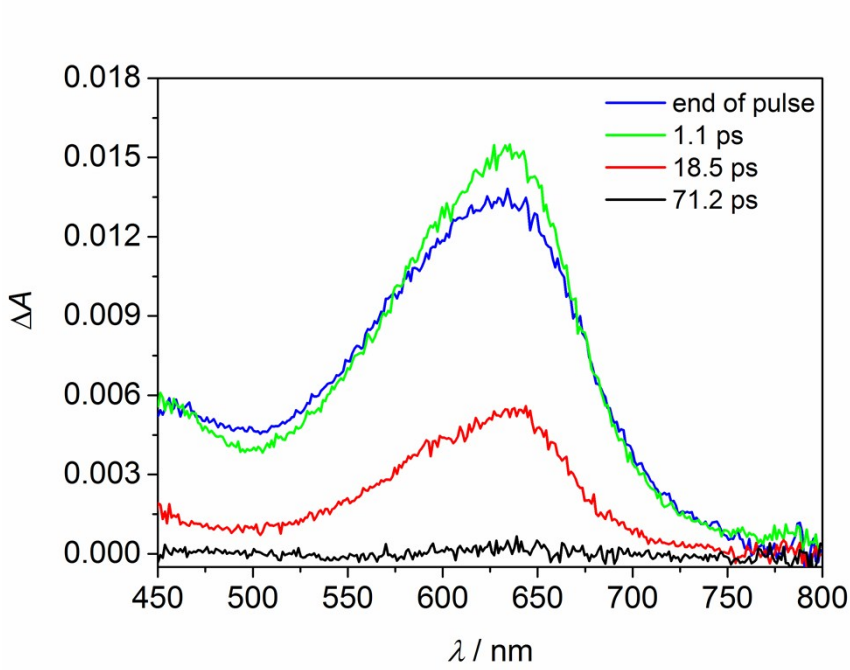


Figure S3: Transient absorption spectra of a DCM solution of **4** at various delays after the pulse. Excitation at 350 nm (A_{350} = 0.2, 0.2 cm optical path).

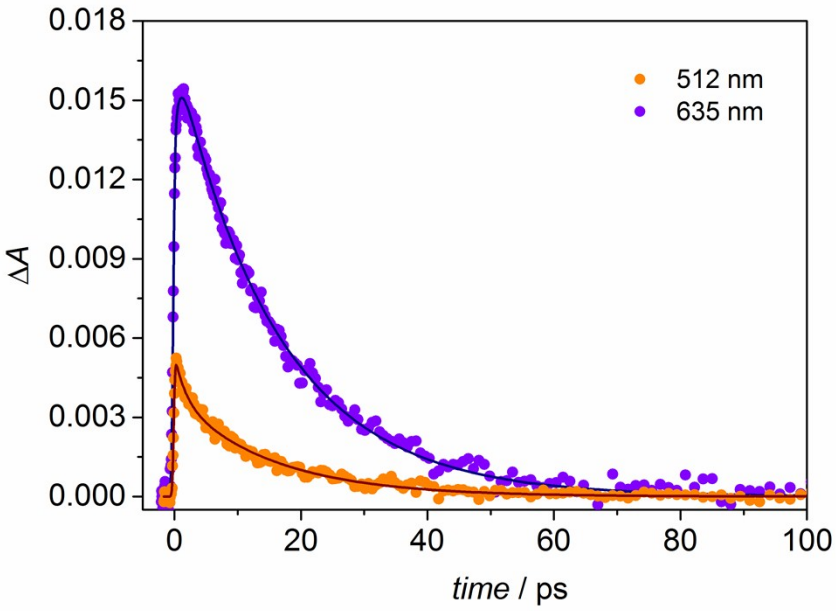
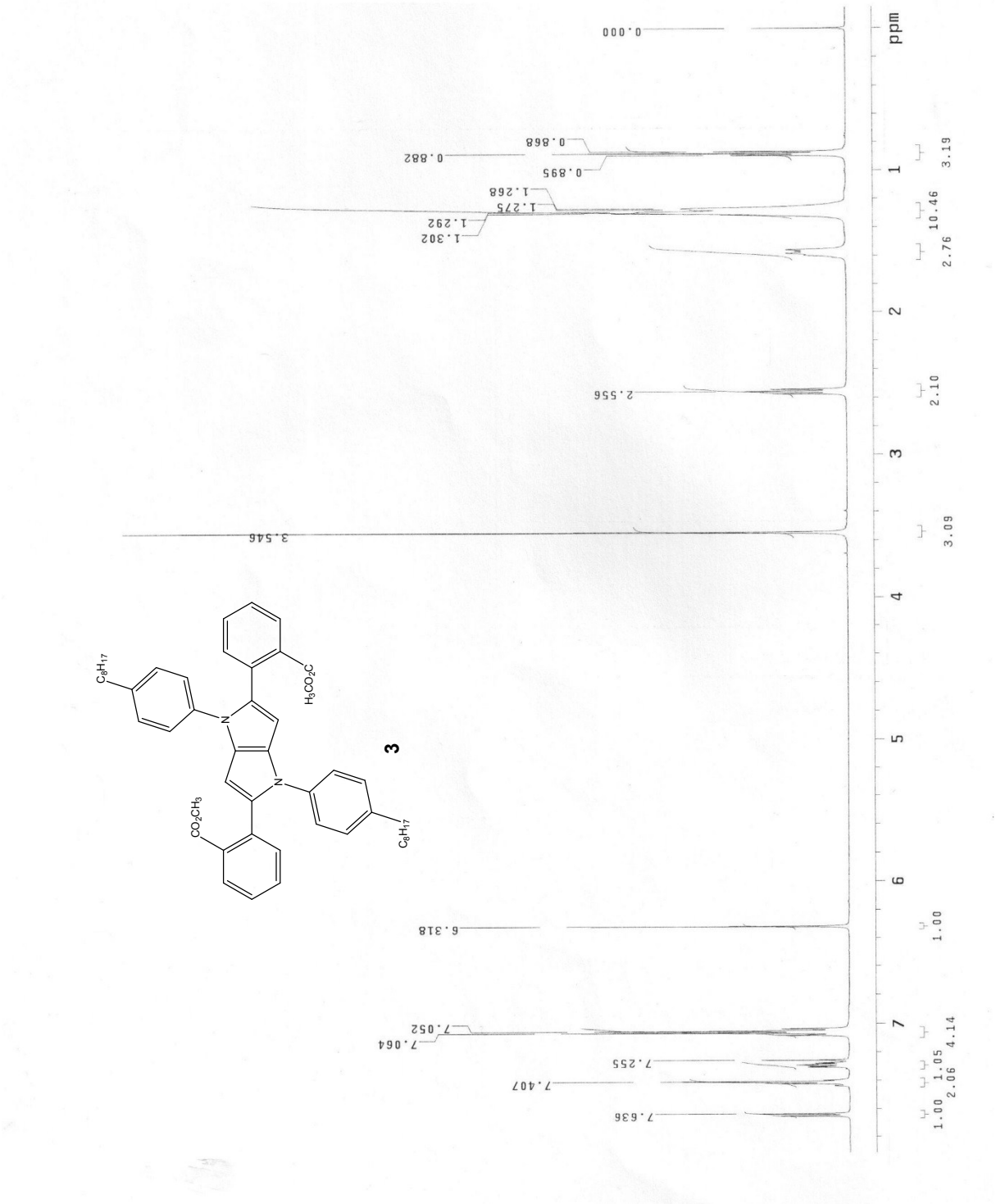
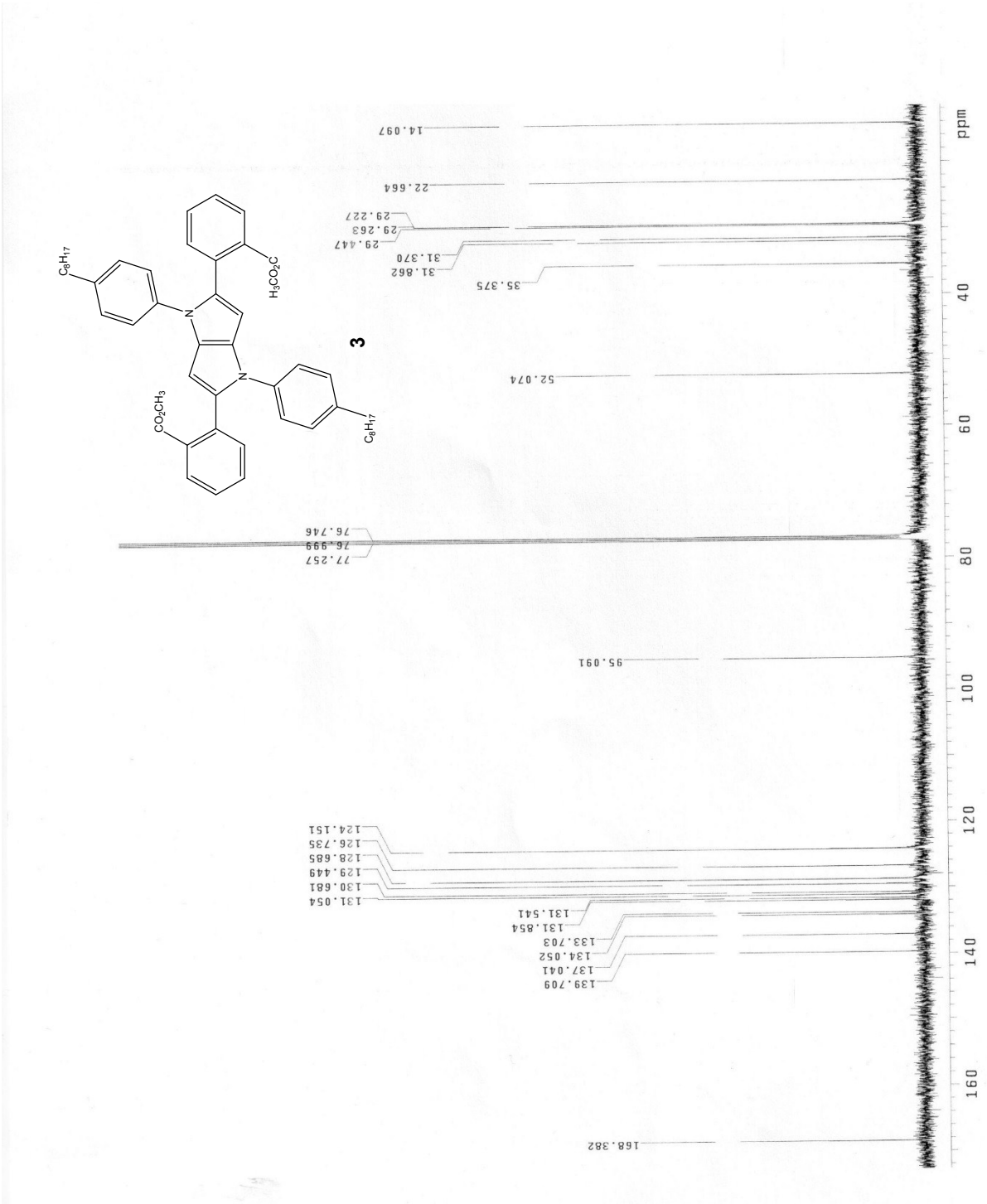
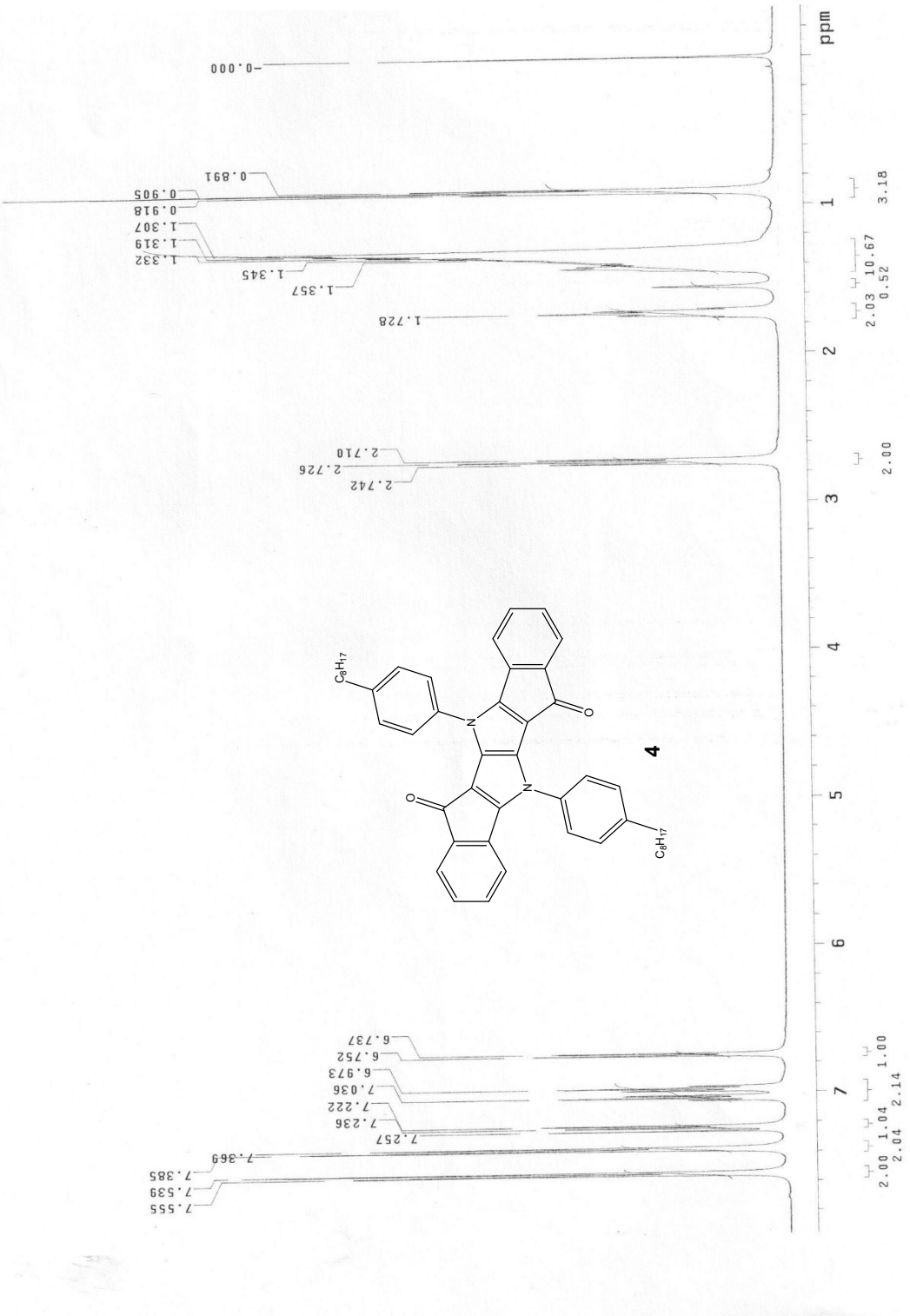


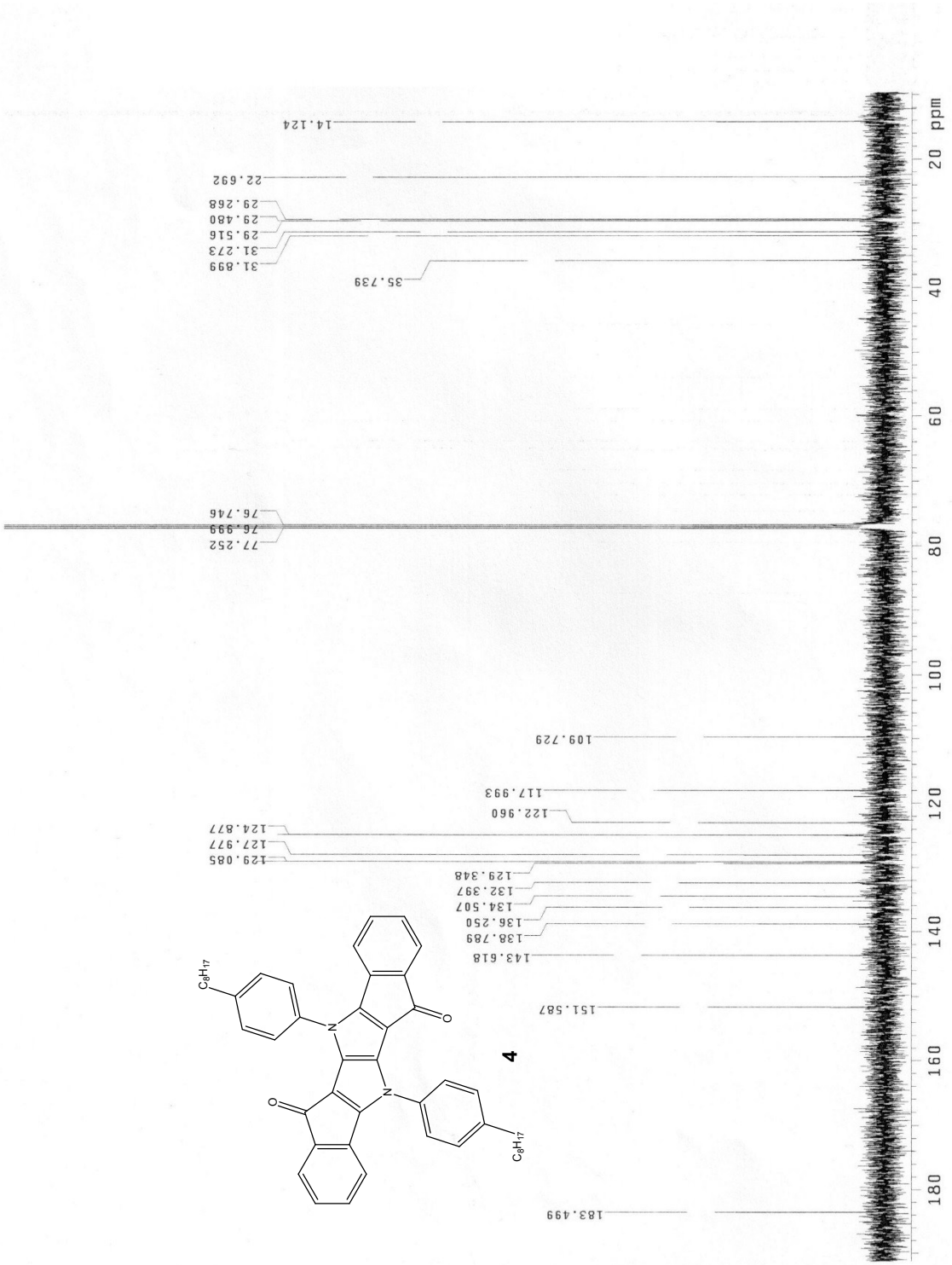
Figure S4: Transient absorption profiles at the indicated wavelengths of a DCM solution of **4** upon excitation at 350 nm (A_{350} = 0.2, 0.2 cm optical path). The fittings are reported as lines.

2. ^{1}H NMR spectra for synthesized compounds




3
14.097
22.664
29.227
29.263
29.447
31.370
31.862
35.375
52.074
76.746
76.999
77.257
95.091
124.151
126.735
128.685
129.449
130.681
131.054
131.541
131.854
133.703
134.052
137.041
139.709
168.382
ppm


7.555
7.539
7.385
7.369
7.257
7.236
7.222
7.036
6.973
6.752
6.737
2.742
2.726
2.710
1.728
1.357
1.345
1.332
1.319
1.307
0.918
0.905
0.891
0.000
ppm
4
C_8H_{17}
C_8H_{17}
O
O
N
N


14.124
22.692
29.268
29.480
29.516
31.273
31.899
35.739
76.746
76.999
77.252
109.729
117.993
122.960
124.877
127.977
129.085
129.348
132.397
134.507
136.250
138.789
143.618
151.587
183.499
ppm
20
40
60
80
100
120
140
160
180
4
C_8H_{17}
C_8H_{17}
N
N
O
O

3. Additional data from the computational study

All electronic calculations were performed with Gaussian 09 (release D01)[1] apart from TPA calculations that were run with DALTON 2016.[2]

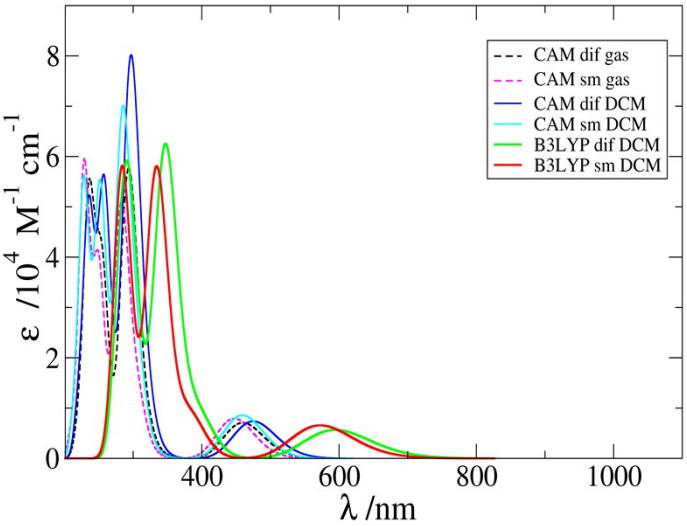


Figure S5a. The computed spectra in DCM reported in the main text and obtained with CAM-B3LYP (CAM) and B3LYP and 2 different basis sets: sm=6-31G(d), dif=6-311+G(d,p), are compared with those predicted in gas phase with CAM-B3LYP and the same two basis sets. Stick transitions were broadened with a phenomenological Gaussian with HWHM=0.2 eV.

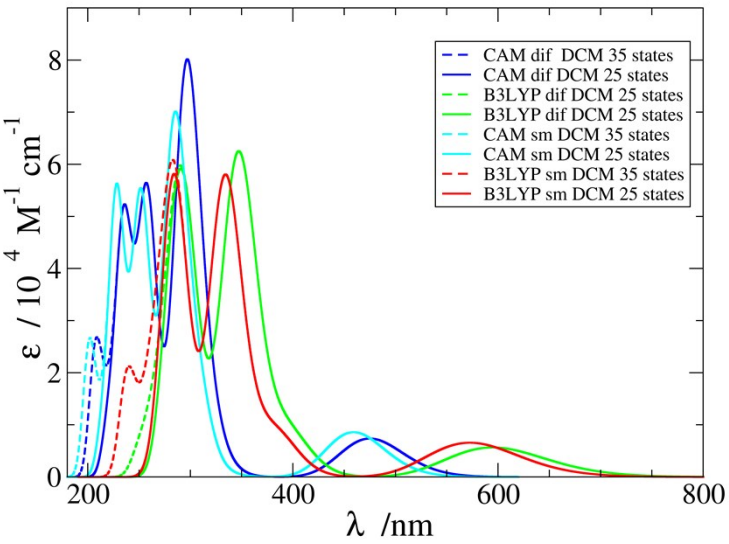


Figure S5b. Convergence test for the computed spectra in DCM with either CAM-B3LYP (CAM) or B3LYP and 2 different basis sets: sm=6-31G(d), dif=6-311+G(d,p). The spectra reported in the main text, obtained including the fist 25 states (solid lines) are compared with those obtained considering the first 35 states (dashed lines). The excitation wavlenght of the 35th state is 206 nm (6-311+G(d,p)) and 193 nm (6-31G(d)) for CAM-B3LYP, and 246 nm (6-311+G(d,p)) and 236 nm (6-31G(d)) for B3LYP. Stick transitions were broadened with a phenomenological Gaussian with HWHM=0.2 eV.

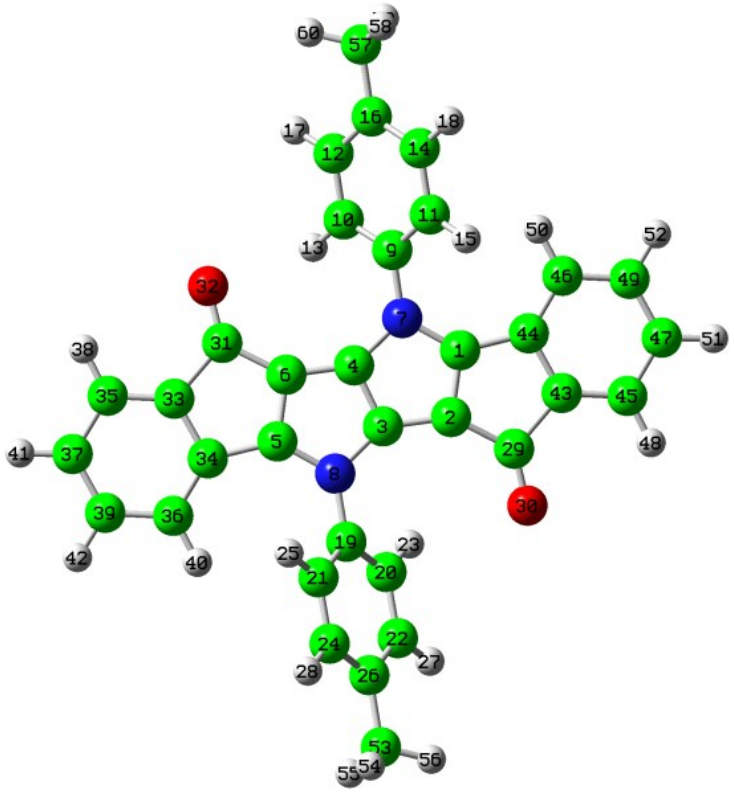


Figure S6. The model molecular structure investigated theoretically with atom labels. The left (L), central (C) and right (R) parts of the molecule, defined in order to discuss the results Mulliken population analysis comprise the following atoms: C (1-8, 9-18, 57-60, 19-28, 53-55), L (31-42), R (29-30, 43-52). The Figure reports a C_2 structure. The rotation of the phenyl rings with respect to the fused rings can be measured with the equivalent torsional angles 20-19-8-3 and 10-9-7-4 which are (absolute values) ~49° and ~55° for CAM-B3LYP/6-311G(d,p) in gas phase and in DCM and ~55° for B3LYP/6-311G(d,p) in DCM. C_i structures are different only for the rotation of one of the two phenyl rings. In this case in fact the equivalent angles are 20-19-8-3 and 11-9-7-4 and they are ~49° and ~56° for CAM-B3LYP/6-311G(d,p) in gas phase and in DCM and ~58° for B3LYP/6-311G(d,p) in DCM

Table S1. Vertical excitation wavelengths (nm) and oscillator strengths (in parenthesis) for the B states of 4 in gas phase and in DCM*.

STATE	GAS			DCM					
	CAM-B3LYP			CAM-B3LYP			B3LYP		
	6-311G(d,p)	6-31G(d)	6-311+G(d,p)	6-311G(d,p)	6-31G(d)	6-311+G(d,p)	6-311G(d,p)	6-31G(d)	6-311+G(d,p)
1B	454 (0.11)	449 (0.12)	461 (0.11)	466 (0.12)	461 (0.13)	477 (0.11)	582 (0.09)	576 (0.10)	599 (0.08)
2B	342 (0.004)	345 (0.003)	342 (0.006)	335 (0.009)	338 (0.006)	334 (0.02)	389 (0.11)	386 (0.11)	395 (0.13)
3B	309 (0.15)	306 (0.18)	313 (0.14)	309 (0.20)	306 (0.26)	314 (0.20)	366 (0.02)	367 (0.04)	364 (0.01)
4B	288 (0.78)	283 (0.73)	293 (0.81)	291 (1.07)	285 (0.98)	296 (1.10)	342 (0.89)	335 (0.85)	348 (0.91)
5B	253 (0.53)	250 (0.55)	255 (0.54)	255 (0.74)	253 (0.76)	259 (0.76)	306 (0.03)	304 (0.04)	311 (0.04)
6B	243 (0.04)	241 (0.03)	246 (0.03)	245 (0.09)	243 (0.09)	249 (0.10)	304 (0.003)	299 (0.03)	308 (0.00)
7B	239 (0.05)	234 (0.05)	242 (0.06)	236 (0.05)	232 (0.05)	239 (0.05)	302 (0.04)	298 (0.002)	306 (0.03)
8B	235 (0.10)	231 (0.18)	239 (0.05)	234 (0.20)	231 (0.22)	238 (0.13)	295 (0.12)	292 (0.08)	302 (0.14)
9B	234 (0.25)	230 (0.29)	237 (0.24)	232 (0.22)	228 (0.50)	236 (0.17)	294 (0.03)	291 (0.07)	299 (0.01)
10B	231 (0.41)	227 (0.32)	235 (0.39)	231 (0.30)	227 (0.02)	234 (0.35)	289 (0.38)	287 (0.30)	294 (0.46)
11B	223 (0.09)	220 (0.07)	226 (0.10)	223 (0.03)	220 (0.03)	226 (0.03)	283 (0.24)	282 (0.34)	285 (0.20)

*molecular structures optimized with 6-311G(d,p) basis set.

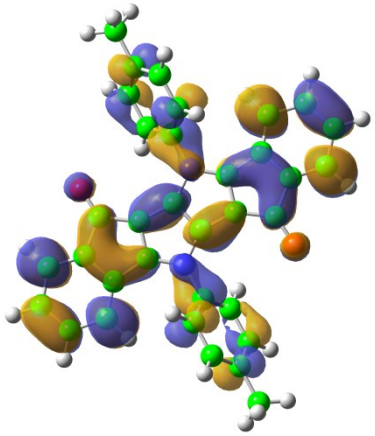


Figure S7. Kohn-Sham Molecular Orbital LUMO+2 computed in DCM at CAM-B3LYP/6-31G(d) level of theory at the symmetric C2v geometry of the GS. Notice that HOMO and LUMO+2 computed in the same conditions with B3LYP functional are extremely similar to the CAM-B3LYP ones reported here (LUMO+2) or in figure 3 in the main text (HOMO).

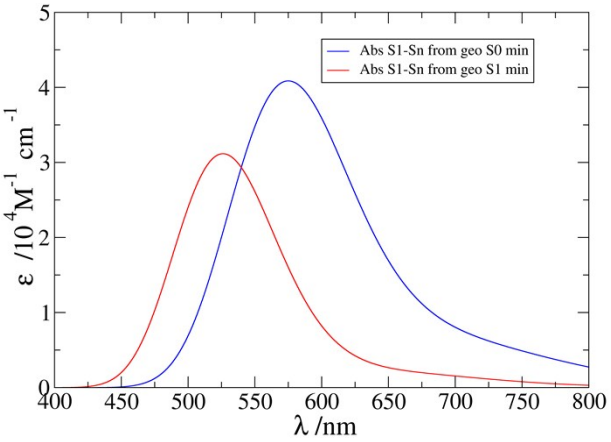


Figure S8. Excited state absorption from S_1 computed with quadratic response in Dalton from double residues at CAM-B3LYP/6-31G(d) level of theory in PCM (nonequilibrium regime), from the geometries of the S0 minimum (C2 symmetry) and of the S1 global minimum. The decay of the computed spectra at short wavelengths is due to the limited number of considered excited states (generically indicated as S_n). For calculations in C2 symmetry the first 5 A excited states were computed, while for the computation from the S1 minimum (C1 symmetry) 8 excited states were included.

Cartesian Coordinates of S0 minimum in gas phase optimized at CAM-B3LYP/6-311G(d,p) level of theory.
Absolute energy -1568.34150764 hartree

6	-0.017843	2.108116	-0.031135
6	1.136208	1.339953	-0.039938
6	0.695928	-0.005560	-0.066430
6	-0.695928	0.005560	-0.066430
6	0.017843	-2.108116	-0.031135
6	-1.136208	-1.339953	-0.039938
7	-1.136208	1.322080	-0.031686
7	1.136208	-1.322080	-0.031686
6	-2.493131	1.740352	0.086772
6	-3.463359	1.191038	-0.738654
6	-2.850148	2.666916	1.056501
6	-4.782789	1.584871	-0.598277
1	-3.192748	0.442273	-1.469988
6	-4.172471	3.065847	1.171908
1	-2.097501	3.059250	1.728691
6	-5.160120	2.534802	0.347306
1	-5.535337	1.136744	-1.236745
1	-4.442888	3.788193	1.933873
6	2.493131	-1.740352	0.086772
6	3.463359	-1.191038	-0.738654
6	2.850148	-2.666916	1.056501
6	4.782789	-1.584871	-0.598277
1	3.192748	-0.442273	-1.469988
6	4.172471	-3.065847	1.171908
1	2.097501	-3.059250	1.728691
6	5.160120	-2.534802	0.347306
1	5.535337	-1.136744	-1.236745
1	4.442888	-3.788193	1.933873
6	2.297767	2.234661	-0.139520
8	3.474733	1.977674	-0.220095
6	-2.297767	-2.234661	-0.139520
8	-3.474733	-1.977674	-0.220095
6	-1.696985	-3.623773	-0.169071
6	-0.292556	-3.543938	-0.123946
6	-2.349249	-4.824937	-0.265616
6	0.463738	-4.695298	-0.198976
6	-1.583628	-5.995209	-0.326034
1	-3.431898	-4.850326	-0.302595
6	-0.202962	-5.923081	-0.298684
1	1.544544	-4.664334	-0.188056
1	-2.072535	-6.958529	-0.402812
1	0.380729	-6.834100	-0.357636
6	1.696985	3.623773	-0.169071
6	0.292556	3.543938	-0.123946
6	2.349249	4.824937	-0.265616
6	-0.463738	4.695298	-0.198976
6	1.583628	5.995209	-0.326034
1	3.431898	4.850326	-0.302595
6	0.202962	5.923081	-0.298684
1	-1.544544	4.664334	-0.188056
1	2.072535	6.958529	-0.402812
1	-0.380729	6.834100	-0.357636
6	6.593801	-2.975444	0.466790
1	6.791019	-3.426928	1.439886
1	6.839591	-3.717311	-0.298306
1	7.277447	-2.134584	0.338291
6	-6.593801	2.975444	0.466790
1	-6.791019	3.426928	1.439886
1	-6.839591	3.717311	-0.298306
1	-7.277447	2.134584	0.338291

Cartesian Coordinates of S0 minimum optimized at CAM-B3LYP/6-311G(d,p) level of theory in dichloromethane with PCM. Absolute energy -1568.35430066 hartree

6	-1.375400	1.596279	0.004758
6	0.002813	1.757155	-0.001268
6	0.535522	0.444746	-0.037749
6	-0.535522	-0.444746	-0.037749
6	1.375400	-1.596279	0.004758
6	-0.002813	-1.757155	-0.001268
7	-1.720589	0.277189	-0.007093
7	1.720589	-0.277189	-0.007093
6	-3.034973	-0.277230	0.039630
6	-3.431019	-1.195072	-0.922344
6	-3.903850	0.085368	1.058920
6	-4.704355	-1.737431	-0.865227
1	-2.744358	-1.484937	-1.706910
6	-5.180067	-0.455177	1.095430
1	-3.577671	0.777112	1.825555
6	-5.602368	-1.372487	0.135931
1	-5.005550	-2.459100	-1.615780
1	-5.853502	-0.169254	1.895254
6	3.034973	0.277230	0.039630
6	3.431019	1.195072	-0.922344
6	3.903850	-0.085368	1.058920
6	4.704355	1.737431	-0.865227
1	2.744358	1.484937	-1.706910
6	5.180067	0.455177	1.095430
1	3.577671	-0.777112	1.825555
6	5.602368	1.372487	0.135931
1	5.005550	2.459100	-1.615780
1	5.853502	0.169254	1.895254
6	0.307583	3.189986	-0.040349
8	1.375400	3.759913	-0.067571
6	-0.307583	-3.189986	-0.040349
8	-1.375400	-3.759913	-0.067571
6	1.048457	-3.863685	-0.059812
6	2.068257	-2.892848	-0.044746
6	1.331861	-5.204142	-0.106949
6	3.390867	-3.279179	-0.092750
6	2.675165	-5.599971	-0.146368
1	0.529819	-5.932662	-0.119009
6	3.680280	-4.649824	-0.143074
1	4.193933	-2.554984	-0.093459
1	2.927087	-6.652384	-0.184391
1	4.715482	-4.966935	-0.180380
6	-1.048457	3.863685	-0.059812
6	-2.068257	2.892848	-0.044746
6	-1.331861	5.204142	-0.106949
6	-3.390867	3.279179	-0.092750
6	-2.675165	5.599971	-0.146368
1	-0.529819	5.932662	-0.119009
6	-3.680280	4.649824	-0.143074
1	-4.193933	2.554984	-0.093459
1	-2.927087	6.652384	-0.184391
1	-4.715482	4.966935	-0.180380
6	6.994058	1.942880	0.168320
1	7.407001	1.923143	1.177476
1	7.664441	1.365299	-0.474298
1	7.007202	2.973818	-0.187966
6	-6.994058	-1.942880	0.168320
1	-7.407001	-1.923143	1.177476
1	-7.664441	-1.365299	-0.474298
1	-7.007202	-2.973818	-0.187966

Cartesian Coordinates of S0 minimum optimized at B3LYP/6-311G(d,p) level of theory in dichloromethane with PCM. Absolute energy -1569.19509968 hartree

6	1.281278	1.684933	0.020377
6	1.725579	0.358498	0.015257
6	0.551328	-0.434137	-0.026986
6	-0.551328	0.434137	-0.026986
6	-1.281278	-1.684933	0.020377
6	-1.725579	-0.358498	0.015257
7	-0.088735	1.747806	0.004771
7	0.088735	-1.747806	0.004771
6	-0.906195	2.923222	0.035864
6	-1.852396	3.136360	-0.964645
6	-0.767643	3.841567	1.075709
6	-2.647789	4.276744	-0.925737
1	-1.964046	2.416223	-1.765396
6	-1.563119	4.983152	1.095145
1	-0.053826	3.656059	1.869216
6	-2.514277	5.222924	0.096729
1	-3.384322	4.432308	-1.706395
1	-1.451143	5.690339	1.909875
6	0.906195	-2.923222	0.035864
6	1.852396	-3.136360	-0.964645
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6	-3.573201	-1.824724	-0.039075
6	-2.405688	-2.627084	-0.028840
6	-4.830899	-2.383639	-0.085532
6	-2.514277	-4.008283	-0.079886
6	-4.942773	-3.785243	-0.129748
1	-5.710483	-1.749651	-0.093868
6	-3.800516	-4.576209	-0.130443
1	-1.639981	-4.645712	-0.083028
1	-5.921574	-4.248350	-0.167905
1	-3.896820	-5.655233	-0.170683
6	3.573201	1.824724	-0.039075
6	2.405688	2.627084	-0.028840
6	4.830899	2.383639	-0.085532
6	2.514277	4.008283	-0.079886
6	4.942773	3.785243	-0.129748
1	5.710483	1.749651	-0.093868
6	3.800516	4.576209	-0.130443
1	1.639981	4.645712	-0.083028
1	5.921574	4.248350	-0.167905
1	3.896820	5.655233	-0.170683
6	3.357748	-6.473920	0.112099
1	3.528438	-6.825749	1.131624
1	2.862834	-7.283343	-0.435385
1	4.327606	-6.304942	-0.360059
6	-3.357748	6.473920	0.112099
1	-3.528438	6.825749	1.131624
1	-2.862834	7.283343	-0.435385
1	-4.327606	6.304942	-0.360059

Cartesian Coordinates of S0 minimum optimized at CAM-B3LYP/6-31G(d) level of theory in dichloromethane with PCM. Absolute energy -1567.98541342 hartree

6	1.281136	1.676273	0.016955
6	1.721384	0.358238	0.013563
6	0.545861	-0.433190	-0.021576
6	-0.545861	0.433190	-0.021576
6	-1.281136	-1.676273	0.016955
6	-1.721384	-0.358238	0.013563
7	-0.084070	1.742771	0.008393
7	0.084070	-1.742771	0.008393
6	-0.902360	2.909120	0.055006
6	-1.947362	3.054610	-0.850072
6	-0.672545	3.883328	1.021401
6	-2.749600	4.186254	-0.791712
1	-2.134304	2.284915	-1.589950
6	-1.473800	5.016858	1.056079
1	0.119393	3.746054	1.750052
6	-2.522540	5.189784	0.151000
1	-3.567595	4.291388	-1.498234
1	-1.289330	5.773147	1.813442
6	0.902360	-2.909120	0.055006
6	1.947362	-3.054610	-0.850072
6	0.672545	-3.883328	1.021401
6	2.749600	-4.186254	-0.791712
1	2.134304	-2.284915	-1.589950
6	1.473800	-5.016858	1.056079
1	-0.119393	-3.746054	1.750052
6	2.522540	-5.189784	0.151000
1	3.567595	-4.291388	-1.498234
1	1.289330	-5.773147	1.813442
6	3.186611	0.353758	-0.041221
8	3.966370	-0.580540	-0.072954
6	-3.186611	-0.353758	-0.041221
8	-3.966370	0.580540	-0.072954
6	-3.569213	-1.816945	-0.071694
6	-2.409919	-2.620466	-0.051537
6	-4.827141	-2.364823	-0.137989
6	-2.522540	-3.995770	-0.113977
6	-4.944359	-3.761739	-0.192047
1	-5.702451	-1.722948	-0.154156
6	-3.808105	-4.555714	-0.184243
1	-1.650327	-4.638457	-0.111780
1	-5.925801	-4.221100	-0.245606
1	-3.908204	-5.635381	-0.233493
6	3.569213	1.816945	-0.071694
6	2.409919	2.620466	-0.051537
6	4.827141	2.364823	-0.137989
6	2.522540	3.995770	-0.113977
6	4.944359	3.761739	-0.192047
1	5.702451	1.722948	-0.154156
6	3.808105	4.555714	-0.184243
1	1.650327	4.638457	-0.111780
1	5.925801	4.221100	-0.245606
1	3.908204	5.635381	-0.233493
6	3.374259	-6.431369	0.181647
1	3.461885	-6.829463	1.196166
1	2.939331	-7.220508	-0.442461
1	4.380522	-6.233097	-0.196616
6	-3.374259	6.431369	0.181647
1	-3.461885	6.829463	1.196166
1	-2.939331	7.220508	-0.442461
1	-4.380522	6.233097	-0.196616

Cartesian Coordinates of S1 transition state (C2 symmetry) optimized at CAM-B3LYP/6-31G(d) level of theory in gas phase. Absolute energy -1567.88594414 hartree. One imaginary frequency with value i1371.1049

6	1.293565	1.664307	-0.045160
6	1.721787	0.297682	-0.041523
6	0.554340	-0.450087	-0.033302
6	-0.554340	0.450087	-0.033302
6	-1.293565	-1.664307	-0.045160
6	-1.721787	-0.297682	-0.041523
7	-0.073468	1.751810	-0.021863
7	0.073468	-1.751810	-0.021863
6	-0.864156	2.930094	0.115118
6	-2.017354	3.088785	-0.644002
6	-0.493613	3.902938	1.038837
6	-2.784418	4.233567	-0.483276
1	-2.335236	2.313548	-1.329029
6	-1.262480	5.050416	1.171722
1	0.381386	3.750893	1.661556
6	-2.417373	5.238150	0.411659
1	-3.693149	4.341671	-1.067670
1	-0.969001	5.804793	1.896218
6	0.864156	-2.930094	0.115118
6	2.017354	-3.088785	-0.644002
6	0.493613	-3.902938	1.038837
6	2.784418	-4.233567	-0.483276
1	2.335236	-2.313548	-1.329029
6	1.262480	-5.050416	1.171722
1	-0.381386	-3.750893	1.661556
6	2.417373	-5.238150	0.411659
1	3.693149	-4.341671	-1.067670
1	0.969001	-5.804793	1.896218
6	3.191006	0.259980	-0.146949
8	3.944123	-0.709372	-0.204796
6	-3.191006	-0.259980	-0.146949
8	-3.944123	0.709372	-0.204796
6	-3.569410	-1.686504	-0.208909
6	-2.417373	-2.537452	-0.160743
6	-4.843494	-2.221581	-0.338022
6	-2.577974	-3.926792	-0.266577
6	-4.985381	-3.597625	-0.428529
1	-5.698598	-1.554161	-0.372876
6	-3.857201	-4.437514	-0.398393
1	-1.721922	-4.590768	-0.251680
1	-5.972803	-4.036562	-0.530650
1	-3.993052	-5.511206	-0.482228
6	3.569410	1.686504	-0.208909
6	2.417373	2.537452	-0.160743
6	4.843494	2.221581	-0.338022
6	2.577974	3.926792	-0.266577
6	4.985381	3.597625	-0.428529
1	5.698598	1.554161	-0.372876
6	3.857201	4.437514	-0.398393
1	1.721922	4.590768	-0.251680
1	5.972803	4.036562	-0.530650
1	3.993052	5.511206	-0.482228
6	3.240860	-6.491620	0.546965
1	3.098116	-6.959875	1.524673
1	2.963606	-7.230206	-0.214215
1	4.307092	-6.282207	0.423817
6	-3.240860	6.491620	0.546965
1	-3.098116	6.959875	1.524673
1	-2.963606	7.230206	-0.214215
1	-4.307092	6.282207	0.423817

Cartesian Coordinates of S1 transition state (C2 symmetry) optimized at CAM-B3LYP/6-31G(d) level of theory in dichloromethane with PCM. Absolute energy -1567.90147046 hartree. One imaginary frequency with value i1270.0298

6	-0.005667	-2.107339	-0.002545
6	-1.180583	-1.286284	0.005941
6	-0.715162	0.018432	-0.004552
6	0.715162	-0.018432	-0.004552
6	0.005667	2.107339	-0.002545
6	1.180583	1.286284	0.005941
7	1.128958	-1.339375	0.004270
7	-1.128958	1.339375	0.004270
6	2.481627	-1.787746	0.071588
6	3.428059	-1.265745	-0.802357
6	2.850202	-2.729583	1.027299
6	4.742758	-1.704734	-0.722690
1	3.142384	-0.516520	-1.530796
6	4.166082	-3.167755	1.083356
1	2.114545	-3.103899	1.731218
6	5.133015	-2.667237	0.209213
1	5.479889	-1.289830	-1.403621
1	4.448890	-3.901400	1.832464
6	-2.481627	1.787746	0.071588
6	-3.428059	1.265745	-0.802357
6	-2.850202	2.729583	1.027299
6	-4.742758	1.704734	-0.722690
1	-3.142384	0.516520	-1.530796
6	-4.166082	3.167755	1.083356
1	-2.114545	3.103899	1.731218
6	-5.133015	2.667237	0.209213
1	-5.479889	1.289830	-1.403621
1	-4.448890	3.901400	1.832464
6	-2.364412	-2.154044	-0.049916
8	-3.557133	-1.845366	-0.064960
6	2.364412	2.154044	-0.049916
8	3.557133	1.845366	-0.064960
6	1.795781	3.517876	-0.103760
6	0.361918	3.483938	-0.083686
6	2.475485	4.724278	-0.189883
6	-0.361918	4.683549	-0.167162
6	1.744879	5.902092	-0.263432
1	3.560835	4.730392	-0.203798
6	0.338127	5.873931	-0.256009
1	-1.445297	4.683992	-0.165013
1	2.257906	6.855788	-0.331876
1	-0.210733	6.807793	-0.321959
6	-1.795781	-3.517876	-0.103760
6	-0.361918	-3.483938	-0.083686
6	-2.475485	-4.724278	-0.189883
6	0.361918	-4.683549	-0.167162
6	-1.744879	-5.902092	-0.263432
1	-3.560835	-4.730392	-0.203798
6	-0.338127	-5.873931	-0.256009
1	1.445297	-4.683992	-0.165013
1	-2.257906	-6.855788	-0.331876
1	0.210733	-6.807793	-0.321959
6	-6.553691	3.163478	0.260875
1	-6.824622	3.491151	1.268054
1	-6.694280	4.018399	-0.410487
1	-7.258145	2.386719	-0.048078
6	6.553691	-3.163478	0.260875
1	6.824622	-3.491151	1.268054
1	6.694280	-4.018399	-0.410487
1	7.258145	-2.386719	-0.048078

Cartesian Coordinates of S1 global mimimum optimized at CAM-B3LYP/6-31G(d) level of theory in dichloromethane with PCM. Absolute energy -1567.90346352 hartree

6	1.308297	1.690235	0.028408
6	1.738974	0.304822	0.038794
6	0.565607	-0.427701	0.026933
6	-0.538048	0.472258	0.021439
6	-1.279267	-1.636571	0.027085
6	-1.704305	-0.289607	0.028955
7	-0.074138	1.773030	0.030435
7	0.071003	-1.731958	0.038225
6	-0.873180	2.949192	0.091866
6	-1.945293	3.106294	-0.779210
6	-0.589220	3.932360	1.036223
6	-2.724678	4.253323	-0.704493
1	-2.172655	2.335529	-1.506342
6	-1.367862	5.080046	1.086083
1	0.228031	3.790190	1.735213
6	-2.446085	5.262532	0.217374
1	-3.564277	4.366422	-1.383908
1	-1.141582	5.841986	1.826325
6	0.861418	-2.921593	0.098076
6	1.900563	-3.103684	-0.806259
6	0.598614	-3.876170	1.074306
6	2.660741	-4.262795	-0.740907
1	2.121500	-2.340667	-1.542698
6	1.361426	-5.035762	1.117298
1	-0.186760	-3.706013	1.803156
6	2.399859	-5.251050	0.209911
1	3.475461	-4.400315	-1.445417
1	1.153973	-5.778729	1.881528
6	3.203018	0.255678	-0.012990
8	3.952006	-0.746172	-0.032179
6	-3.174137	-0.265681	-0.022187
8	-3.938691	0.680177	-0.038418
6	-3.566343	-1.718618	-0.068438
6	-2.419173	-2.544137	-0.047082
6	-4.834026	-2.249790	-0.148369
6	-2.553527	-3.923059	-0.121513
6	-4.968352	-3.640358	-0.215017
1	-5.699878	-1.595822	-0.164241
6	-3.842093	-4.457383	-0.205882
1	-1.690777	-4.577775	-0.116567
1	-5.955477	-4.085623	-0.279001
1	-3.962707	-5.534071	-0.265011
6	3.581267	1.656699	-0.060260
6	2.419360	2.535116	-0.044970
6	4.865595	2.205966	-0.139933
6	2.602634	3.937914	-0.126968
6	5.012179	3.574038	-0.210602
1	5.725748	1.543841	-0.149114
6	3.879174	4.434806	-0.207918
1	1.750262	4.607258	-0.129071
1	6.003631	4.011587	-0.273200
1	4.032750	5.507159	-0.272120
6	3.210342	-6.519448	0.246284
1	3.198327	-6.971688	1.241320
1	2.809947	-7.259373	-0.456195
1	4.250810	-6.334399	-0.033916
6	-3.271973	6.520847	0.264660
1	-3.352209	6.906368	1.284782
1	-2.820005	7.309946	-0.347246
1	-4.281801	6.348735	-0.116690

Cartesian Coordinates of S1 global mimimum optimized at CAM-B3LYP/6-31G(d) level of theory in gas phase. Absolute energy -1567.88821934 hartree

6	1.302568	1.685151	-0.068263
6	1.735408	0.302387	-0.069614
6	0.560289	-0.430424	-0.048313
6	-0.543003	0.465093	-0.048292
6	-1.283475	-1.644640	-0.060452
6	-1.708955	-0.298159	-0.057669
7	-0.078396	1.770637	-0.039764
7	0.067856	-1.738674	-0.034189
6	-0.868220	2.942979	0.114017
6	-2.020858	3.115001	-0.643902
6	-0.497800	3.908011	1.047101
6	-2.791878	4.255167	-0.467049
1	-2.326629	2.355652	-1.352660
6	-1.269015	5.051747	1.195737
1	0.382477	3.752808	1.661517
6	-2.426842	5.247554	0.441861
1	-3.698040	4.373176	-1.053834
1	-0.973592	5.798848	1.927109
6	0.856231	-2.921142	0.115691
6	2.028714	-3.073225	-0.613965
6	0.465928	-3.892868	1.031597
6	2.788403	-4.220548	-0.439542
1	2.381069	-2.286606	-1.267962
6	1.228472	-5.043590	1.176711
1	-0.416521	-3.738949	1.643258
6	2.398140	-5.230221	0.440154
1	3.714401	-4.322319	-0.997143
1	0.919669	-5.798281	1.894386
6	3.200161	0.254676	-0.193756
8	3.943955	-0.743005	-0.279339
6	-3.179326	-0.272910	-0.151940
8	-3.945031	0.667549	-0.199278
6	-3.569279	-1.726639	-0.216473
6	-2.424096	-2.552201	-0.176242
6	-4.835377	-2.250912	-0.342815
6	-2.561766	-3.928600	-0.288148
6	-4.972647	-3.638720	-0.440093
1	-5.693715	-1.587457	-0.373422
6	-3.848573	-4.457253	-0.419327
1	-1.700529	-4.585227	-0.279568
1	-5.958742	-4.080247	-0.540711
1	-3.968798	-5.532373	-0.507801
6	3.569389	1.655363	-0.245741
6	2.411944	2.534515	-0.182341
6	4.850316	2.204326	-0.383904
6	2.588870	3.934550	-0.280769
6	4.991105	3.570409	-0.464977
1	5.703979	1.536092	-0.430329
6	3.860346	4.432433	-0.418313
1	1.735845	4.602750	-0.254153
1	5.978971	4.008219	-0.572634
1	4.010506	5.504518	-0.495939
6	3.220792	-6.482450	0.590204
1	2.992816	-7.001151	1.525205
1	3.027384	-7.182400	-0.230880
1	4.291088	-6.257546	0.579479
6	-3.249476	6.499756	0.594618
1	-3.153921	6.920132	1.599631
1	-2.929289	7.272030	-0.114555
1	-4.309309	6.305551	0.408134

Cartesian Coordinates of S1 global mimimum optimized at CAM-B3LYP/6-311G(d,p) level of theory in dichloromethane with PCM. Absolute energy -1568.27278679 hartree

6	1.306117	1.690441	0.031294
6	1.734801	0.305642	0.039952
6	0.563876	-0.425543	0.024994
6	-0.538924	0.474201	0.018321
6	-1.278030	-1.632412	0.022157
6	-1.703708	-0.287571	0.022290
7	-0.074319	1.772525	0.029572
7	0.068523	-1.727892	0.033249
6	-0.872576	2.951374	0.082865
6	-1.895735	3.136508	-0.835159
6	-0.634231	3.905486	1.064137
6	-2.674260	4.281441	-0.769699
1	-2.085664	2.388349	-1.593377
6	-1.411085	5.051454	1.107365
1	0.147088	3.743374	1.796060
6	-2.442149	5.260671	0.192583
1	-3.476897	4.415117	-1.485640
1	-1.221150	5.790322	1.877533
6	0.856784	-2.921484	0.084606
6	1.816667	-3.152064	-0.888572
6	0.668949	-3.826040	1.118903
6	2.576206	-4.308467	-0.830919
1	1.972290	-2.429975	-1.678701
6	1.430863	-4.983410	1.157552
1	-0.058513	-3.619677	1.894178
6	2.392642	-5.245458	0.184226
1	3.330172	-4.483079	-1.589471
1	1.283680	-5.686891	1.968724
6	3.197423	0.254349	0.001652
8	3.939352	-0.746639	-0.014877
6	-3.172910	-0.264954	-0.023256
8	-3.934238	0.674612	-0.042129
6	-3.562788	-1.720485	-0.060636
6	-2.415037	-2.540405	-0.039044
6	-4.825705	-2.257527	-0.128897
6	-2.541436	-3.918085	-0.100077
6	-4.952794	-3.647160	-0.182916
1	-5.694307	-1.610528	-0.145101
6	-3.825655	-4.458140	-0.172252
1	-1.676251	-4.566305	-0.094117
1	-5.936247	-4.096650	-0.237584
1	-3.943000	-5.533614	-0.220786
6	3.578437	1.654089	-0.037129
6	2.417101	2.531828	-0.026064
6	4.860886	2.204803	-0.101283
6	2.599866	3.933379	-0.096130
6	5.005923	3.570877	-0.160808
1	5.721430	1.546393	-0.107382
6	3.873966	4.430530	-0.161851
1	1.748893	4.601196	-0.101383
1	5.995765	4.008397	-0.211289
1	4.027987	5.501181	-0.216828
6	3.203056	-6.512065	0.217922
1	3.273498	-6.911027	1.230311
1	2.743744	-7.281099	-0.409404
1	4.213583	-6.344301	-0.156807
6	-3.266756	6.518139	0.234230
1	-3.398477	6.871400	1.257937
1	-2.779984	7.319376	-0.328861
1	-4.252746	6.359837	-0.203837

Cartesian Coordinates of S1 global mimimum optimized at B3LYP/6-311G(d,p) level of theory in dichloromethane with PCM. Absolute energy -1569.12880656 hartree

6	1.304369	1.680817	0.042289
6	1.736909	0.301235	0.048517
6	0.563942	-0.434895	0.031892
6	-0.551058	0.467985	0.030309
6	-1.286946	-1.652983	0.040238
6	-1.714918	-0.291370	0.044685
7	-0.077054	1.771702	0.040606
7	0.070103	-1.743098	0.041415
6	-0.873497	2.959222	0.079678
6	-1.839133	3.180790	-0.900301
6	-0.691779	3.887288	1.105619
6	-2.614584	4.335159	-0.852405
1	-1.981990	2.457993	-1.693659
6	-1.466395	5.041898	1.132933
1	0.040521	3.698916	1.881360
6	-2.439262	5.288447	0.156111
1	-3.366901	4.496289	-1.616692
1	-1.321060	5.755831	1.936526
6	0.863206	-2.939097	0.080274
6	1.795897	-3.181558	-0.924741
6	0.707155	-3.839978	1.132182
6	2.558944	-4.343293	-0.881138
1	1.925163	-2.469165	-1.729084
6	1.473240	-5.000995	1.157192
1	0.005387	-3.627065	1.929628
6	2.408016	-5.275352	0.151849
1	3.286734	-4.524716	-1.664094
1	1.351052	-5.696224	1.980498
6	3.210982	0.258525	0.014819
8	3.961171	-0.743686	0.000081
6	-3.188738	-0.267033	0.013683
8	-3.949755	0.684279	0.007661
6	-3.577717	-1.721079	-0.025299
6	-2.419584	-2.550303	-0.014865
6	-4.846038	-2.264681	-0.085479
6	-2.553418	-3.937616	-0.077970
6	-4.974690	-3.658407	-0.142688
1	-5.716429	-1.618915	-0.093035
6	-3.841210	-4.476342	-0.142447
1	-1.688590	-4.587206	-0.078871
1	-5.959326	-4.107567	-0.191075
1	-3.961426	-5.552058	-0.192784
6	3.589403	1.667448	-0.019728
6	2.423154	2.541467	-0.008470
6	4.869360	2.231152	-0.079282
6	2.588228	3.940464	-0.070787
6	5.003698	3.609581	-0.134153
1	5.738737	1.583196	-0.086542
6	3.868057	4.460534	-0.133264
1	1.729200	4.599335	-0.072242
1	5.992382	4.052519	-0.181376
1	4.009293	5.533739	-0.182269
6	3.217798	-6.547928	0.172954
1	3.400957	-6.885503	1.195078
1	2.688651	-7.352966	-0.348348
1	4.180983	-6.413923	-0.323102
6	-3.258136	6.555432	0.181665
1	-3.466170	6.873301	1.205735
1	-2.723384	7.374281	-0.311625
1	-4.209506	6.424521	-0.337313

4. References

[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision D.01.; Gaussian, Inc.: Wallingford, CT, 2009.

[2] Aidas K, Angeli C, Bak KL, Bakken V, Bast R, Boman L, Christiansen O, Cimiraglia R, Coriani S, Dahle P, Dalskov EK, Ekström U, Enevoldsen T, Eriksen JJ, Ettenhuber P, Fernández B, Ferrighi L, Fliegl H, Frediani L, Hald K, Halkier A, Hättig C, Heiberg H, Helgaker T, Hennum AC, Hettema H, Hjertenæs E, Høst S, Høyvik IM, Iozzi MF, Jansík B, Jensen HJ, Jonsson D, Jørgensen P, Kauczor J, Kirpekar S, Kjærgaard T, Klopper W, Knecht S, Kobayashi R, Koch H, Kongsted J, Krapp A, Kristensen K, Ligabue A, Lutnæs OB, Melo JI, Mikkelsen KV, Myhre RH, Neiss C, Nielsen CB, Norman P, Olsen J, Olsen JM, Osted A, Packer MJ, Pawlowski F, Pedersen TB, Provasi PF, Reine S, Rinkevicius Z, Ruden TA, Ruud K, Rybkin VV, Sałek P, Samson CC, de Merás AS, Saue T, Sauer SP, Schimmelpfennig B, Sneskov K, Steindal AH, Sylvester-Hvid KO, Taylor PR, Teale AM, Tellgren EI, Tew DP, Thorvaldsen AJ, Thøgersen L, Vahtras O, Watson MA, Wilson DJ, Ziolkowski M, Agren H. Wiley Interdiscip Rev Comput Mol Sci. 2014 May;4(3):269-284.