

Supporting Information

for

Qualitatively Incorrect Features in the TDDFT Spectrum of Thiophene-Based Compounds

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Excitation energies of thiophene, dithienothiophene, thienothiophene and bithiophene.

Table S1. Excitation energies (in eV) and oscillator strengths (in parenthesis) of thiophene and dithienothiophene which are depicted in the Figure 2 of the main text. All the values are converged at cc-pVQZ level, except for EOM-CCSD of dithienothiophene (cc-pVTZ) and the CASPT2 results taken from the literature. We also list tuning parameters (γ) of the range separated functional, the diagnostic parameters for ADC(2) and CC2 and available experimental absorption maxima.

	thiophene		dithienothiophene	
	B ₂	A ₁	B ₂	A ₁
PBE	5.65 (0.073)	5.63 (0.058)	4.04 (0.305)	3.96 (0.059)
B3LYP	5.69 (0.078)	5.79 (0.074)	4.21 (0.333)	4.38 (0.093)
PBE0	5.79 (0.079)	5.89 (0.079)	4.31 (0.340)	4.50 (0.101)
TDA(PBE0)	6.10 (0.104)	6.02 (0.082)	4.54 (0.476)	4.62 (0.130)
M06	5.55 (0.070)	5.77 (0.073)	4.18 (0.303)	4.43 (0.097)
M06-2X	5.92 (0.082)	5.94 (0.096)	4.52 (0.342)	4.77 (0.138)
M06-2X (H ₂ O, IEF-PCM)	5.87 (0.105)	5.92 (0.134)		
ωB97x-D	5.81 (0.082)	5.93 (0.090)	4.46 (0.336)	4.79 (0.139)
LC-PBE	5.98 (0.081)	6.10 (0.113)		
LC-PBE*	5.95 (0.083)	5.99 (0.104)	4.64 (0.336)	4.97 (0.169)
γ	0.38		0.37	
TDA-B2PLYP (no perturbative correction)	6.08	6.23	4.66	5.12
TDA-B2PLYP	6.09 (0.106)	5.83 (0.100)	4.58 (0.461)	4.54 (0.169)
TDHF	5.74 (0.075)	6.47 (0.134)	4.48 (0.299)	5.69 (0.213)
CIS	6.08 (0.101)	6.70 (0.150)	4.79 (0.420)	5.91 (0.276)
CIS(D)	6.30 (-)	5.79 (-)	4.93 (-)	4.61 (-)
ADC(2)	6.12 (0.105)	5.75 (0.093)	4.67 (0.464)	4.59 (0.146)
D ₁	0.029		0.031	
%doubles	7.26	9.45	10.1	11.6
CC2	6.13 (0.094)	5.78 (0.078)	4.68 (0.411)	4.62 (0.130)
D ₁	0.029		0.031	
%doubles	7.39	9.61	10.3	11.8
EOM-CCSD	6.18 (0.085)	5.83 (0.081)	4.88 (0.386)	4.92 (0.153)
SAC-CI	6.06 (0.123)	5.66 (0.099)		
CASPT2	6.14 (0.109) ¹	5.85 (0.067) ¹		
Exp. Max.	5.93 ² ,5.64 ³	5.48 ² ,5.26 ³		

Table S2. Excitation energies (in eV) and oscillator strengths (in parenthesis) of thienothiophene and bithiophene which are depicted in the Figure 3 of the main text. States are described based on the orbital excitations with higher coefficients. Values are computed with the cc-pVQZ basis set, except for EOM-CCSD and SAC-CI of bithiophene (cc-pVTZ) and the CASPT2 results taken from the literature. We also list tuning parameters (γ) of the range separated functional, the diagnostic parameters of ADC(2) and CC2 and available experimental absorption maxima.

	thienothiophene		bithiophene	
	B _u (H-L)	B _u (H-1-L)	B (H-L)	B (H-2-L)
PBE	4.48 (0.141)	4.80 (0.122)	3.80 (0.352)	4.63 (0.030)
B3LYP	4.75 (0.216)	4.97 (0.089)	3.97 (0.371)	5.08 (0.055)
PBE0	4.85 (0.226)	5.08 (0.090)	4.07 (0.380)	5.22 (0.064)
TDA(PBE0)	5.04 (0.255)	5.29 (0.163)	4.29 (0.525)	5.31 (0.066)
M06	4.71 (0.214)	4.95 (0.074)	3.97 (0.355)	5.13 (0.053)
M06-2X	5.04 (0.249)	5.24 (0.097)	4.27 (0.372)	5.50 (0.107)
M06-2X (H ₂ O, IEF-PCM)	4.97 (0.330)	5.23 (0.126)	4.19 (0.450)	5.48 (0.159)
ω B97x-D	4.98 (0.249)	5.20 (0.093)	4.23 (0.378)	5.50 (0.105)
LC-PBE	5.21 (0.245)	5.48 (0.135)	4.49 (0.378)	5.81 (0.153)
LC-PBE*	5.00 (0.236)	5.18 (0.106)	4.24 (0.368)	5.39 (0.103)
γ	0.27		0.245	
TDA-B2PLYP (no perturbative correction)	5.24	5.53	4.24	5.75
TDA-B2PLYP	5.15 (0.324)	5.07 (0.121)	4.33 (0.504)	5.32 (0.085)
TDHF	5.02 (0.203)	5.95 (0.199)	4.35 (0.371)	6.22 (0.154)
CIS	5.34 (0.279)	6.18 (0.237)	4.62 (0.482)	6.40 (0.141)
CIS(D)	5.51 (-)	5.00 (-)	4.67 (-)	5.50 (-)
ADC(2)	5.30 (0.245)	4.96 (0.180)	4.44 (0.450)	5.39 (0.150)
D ₁	0.030		0.033	
%doubles	9.05	10.7	9.52	10.4
CC2	5.31 (0.212)	4.99 (0.165)	4.45 (0.416)	5.42 (0.114)
D ₁	0.030		0.033	
%doubles	9.23	10.9	9.66	10.6
EOM-CCSD	5.42 (0.187)	5.19 (0.177)	4.68 (0.407)	5.60 (0.135)
SAC-CI	5.29 (0.253)	5.04 (0.278)	4.30 (0.494)	5.66 (0.185)
CASPT2			4.11 (0.32) ⁵	5.14 (0.13) ⁵
Exp. Max.			4.31 ⁴	5.08 ⁴

D₁ diagnostics of ADC(2) and CC2 measure the quality of the ground state wavefunction. Values smaller than 0.04 in case of ADC2 (MP2) and 0.05 in case of CC2 indicate that problems with the multireference character should not be expected. However, values as high as 0.10 and 0.15 may be acceptable.⁶ Contributions of excitation levels (singles, doubles) may also be evaluated for each excited state.

Method should be trusted for values of %doubles smaller than 15,⁷ otherwise problems with double excitations can be expected.

Despite the good agreement within wavefunction-based methods for the spectrum of thiophene, there is still a rigid shift of several tenths of eV with respect to experimentally measured absorption maxima. The discussion about the experimental challenges in assignment of thiophene excitations was recently reported in a combined theoretical and experimental study by Holland et al.⁸ While it is now clear that A_1 is the lowest lying transition, earlier experimental studies were ambiguous and even missassigned the relative position of the B_2 and A_1 . The unambiguous interpretation of the spectrum is still undermined by the fact that two peaks largely overlap and that the B_2 state may be unbound. The same study by Holland et al. also confirms the good performance of the EOM-CCSD, SAC-CI and ADC(2) methods. Figure S1 illustrates the good agreement between our ADC(2) spectrum from the Wigner distribution and the experimental cross section from reference 8.

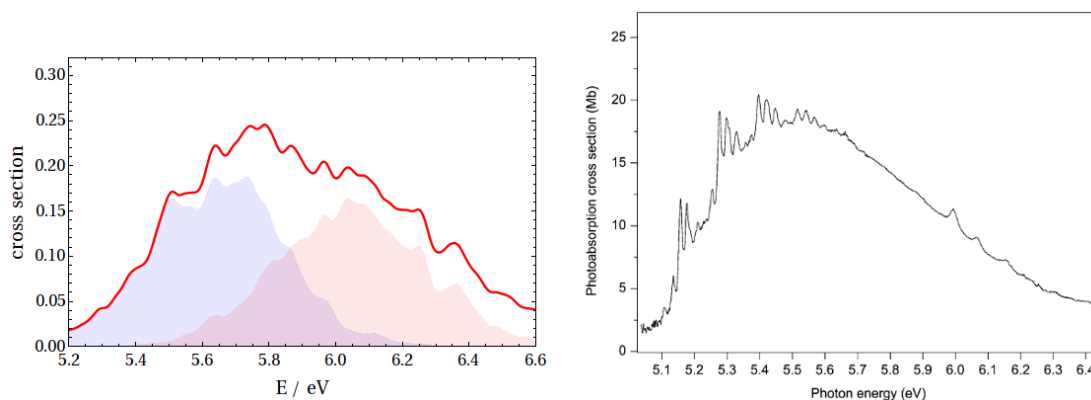


Figure S1. Photoabsorption spectra of thiophene computed with ADC(2) method from Wigner distribution (on the left) and the experimental cross section (on the right). The experimental spectrum was adapted from Reference 8 with permission from the PCCP Owner Societies.

Plot of density differences.

Figure S2. Relaxed density differences between the ground state and the first two excited states of thiophene with PBE0 and ADC(2) (isovalue= ± 0.0005). The cc-pVQZ basis set was used.

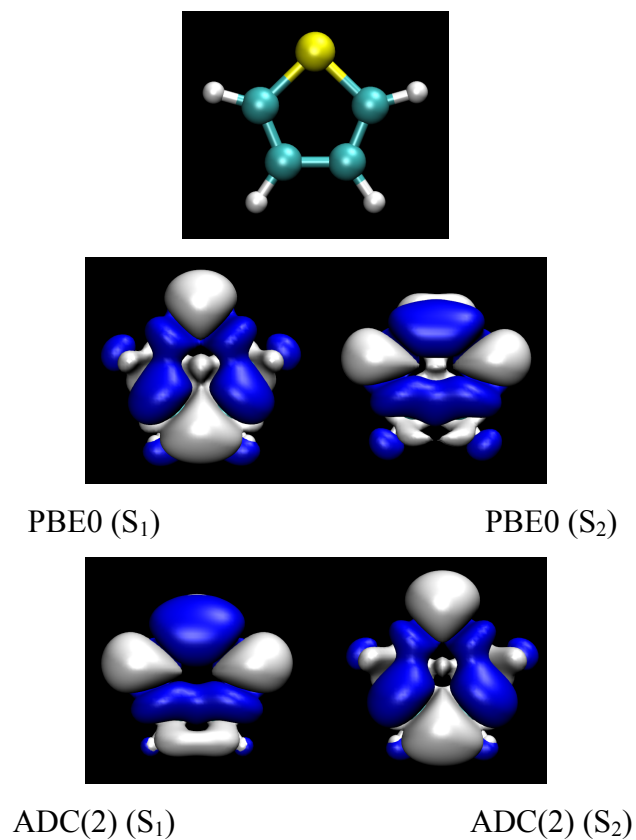
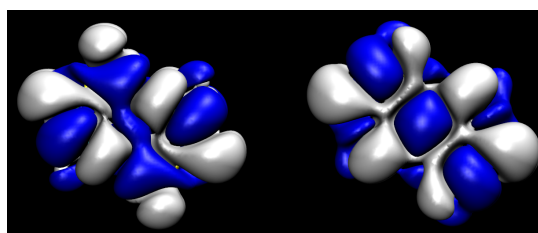
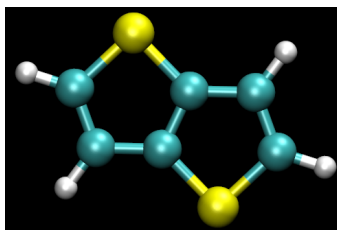
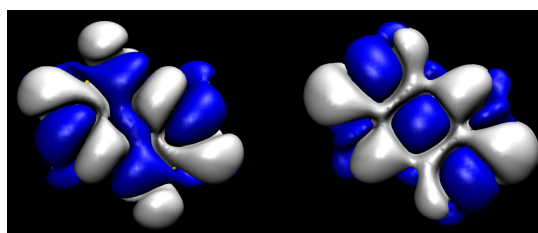


Figure S3. Relaxed density differences between the ground state and the first two excited states of thienothiophene with PBE0, M06-2X, LC-PBE*, CIS and ADC(2) (isovalue= ± 0.0002). The cc-pVQZ basis set was used.



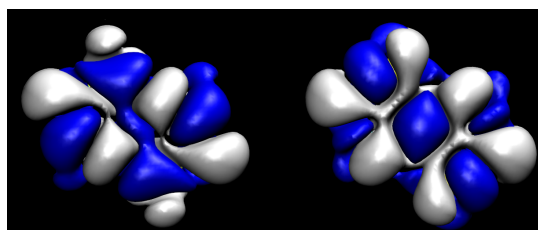
PBE0 (S₁)

PBE0 (S₂)



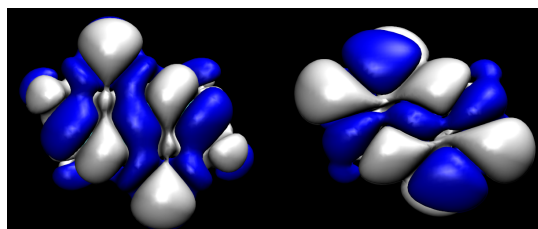
M06-2X (S₁)

M06-2X (S₂)



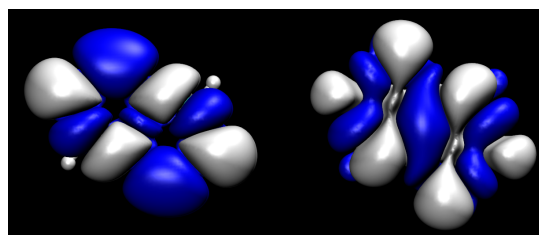
LC-PBE* (S₁)

LC-PBE* (S₂)



CIS (S₁)

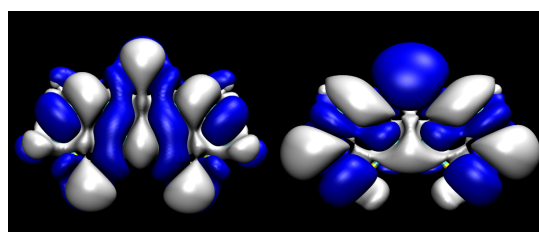
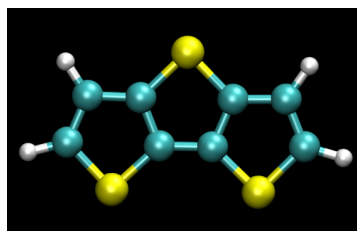
CIS (S₂)



ADC(2) (S_1)

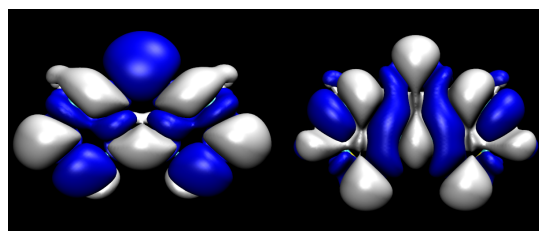
ADC(2) (S_2)

Figure S4. Relaxed density differences between the ground state and the first two excited states of dithienothiophene with PBE0 and ADC(2) (isovalue= ± 0.0002). The cc-pVQZ basis set was used.



PBE0 (S_1)

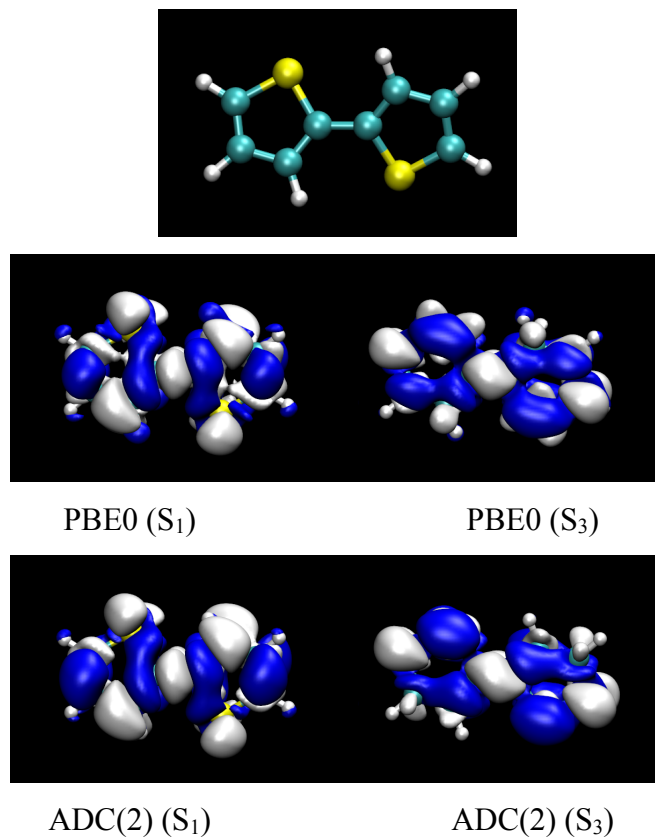
PBE0 (S_2)



ADC(2) (S_1)

ADC(2) (S_2)

Figure S5. Relaxed density differences between the ground state and the S_1 and S_3 states of bithiophene with PBE0 and ADC(2) (isovalue= ± 0.0005). The cc-pVQZ basis set was used.



Structural data for ground and excited state geometries.

Cartesian coordinates (Å) of optimized ground state minima

Thiophene – ground state

C	-0.004024	-1.235762	0.000020
C	-1.265928	-0.712283	-0.000011
C	-1.265928	0.712283	0.000004
C	-0.004024	1.235762	0.000013
S	1.198141	0.000000	0.000036
H	0.289783	-2.277537	0.000028
H	-2.163122	-1.322094	-0.000029
H	-2.163122	1.322094	-0.000006
H	0.289783	2.277537	0.000015

Dithienothiophene – ground state

C	9.934087	12.206173	0.630334
C	8.646135	12.657907	0.616158
C	7.731496	11.611002	0.910264
C	8.343715	10.387296	1.141555
H	8.375589	13.686565	0.405583
C	7.407212	9.361240	1.432489
C	6.098093	9.821404	1.417807
C	5.138038	8.814311	1.706182
C	5.739333	7.610292	1.933928
H	4.064740	8.963325	1.744837
S	10.064150	10.512070	0.998579
H	10.835544	12.775576	0.443421
S	5.989765	11.526893	1.045442
S	7.471890	7.671979	1.804289
H	5.262242	6.669026	2.175222

Thienothiophene – ground state

C	-5.547863	-0.440275	0.354590
C	-5.134714	-1.668850	-0.071224
C	-3.757583	-1.872855	0.220987
S	-4.287600	0.487575	1.112412
C	-3.153003	-0.800555	0.860424
C	-1.775872	-1.004561	1.152636
C	-1.362723	-2.233136	0.726821
S	-2.622987	-3.160986	-0.030999
H	-6.538780	-0.012656	0.267878
H	-5.785707	-2.381443	-0.565146
H	-1.124879	-0.291969	1.646559
H	-0.371809	-2.660758	0.813541

Bithiophene – ground state

C	-5.068050	-0.028063	-0.060010
C	-4.915273	-1.382846	0.021812
C	-3.560177	-1.771434	0.192768
C	-2.692817	-0.706857	0.238609
S	-3.556211	0.793274	0.055357
H	-5.981866	0.538811	-0.183211
H	-5.745349	-2.079138	-0.029944
H	-3.232253	-2.801746	0.300740
C	-1.253529	-0.714428	0.400515
C	-0.427591	0.303013	0.813278
C	0.942284	-0.068861	0.853206
C	1.147364	-1.364257	0.471987
S	-0.329110	-2.145377	0.043623
H	-0.799939	1.282784	1.099801
H	1.743486	0.594623	1.160426
H	2.081472	-1.908164	0.415563

Terthiophene – ground state

C	0.409094	1.812473	-1.308225
C	1.828324	1.796043	-1.322924
C	2.367671	1.759477	-0.068482
H	-0.206508	1.861813	-2.202276
H	2.426954	1.818305	-2.227144
S	1.148946	1.730519	1.151081
C	-0.120466	1.787911	-0.039494
C	-1.508544	1.794886	0.363547
C	-2.050251	2.083993	1.593395
S	-2.761373	1.385451	-0.774874
C	-3.461615	2.000195	1.619761
H	-1.445749	2.376453	2.447552
C	-4.010694	1.646426	0.410258
H	-4.064154	2.220446	2.496694
C	-5.402174	1.474430	0.058973
C	-5.976700	1.429575	-1.189415
S	-6.611929	1.274967	1.295421
C	-7.383706	1.246080	-1.152019
H	-5.404076	1.545903	-2.105543
C	-7.869061	1.153131	0.121400
H	-8.013226	1.192579	-2.033664
H	-8.894093	1.018002	0.441676
H	3.412571	1.745844	0.213540

Furan – ground state

C	0.000000	-0.348270	1.088780
C	0.000000	0.959220	0.715540
C	0.000000	0.959220	-0.715540
C	0.000000	-0.348270	-1.088780
H	0.000000	-0.846940	2.047630
H	0.000000	1.814880	1.376580
H	0.000000	1.814880	-1.376580
H	0.000000	-0.846940	-2.047630
O	0.000000	-1.158410	0.000000

Furofuran – ground state

C	2.063090	-0.032500	0.000000
C	1.307370	-1.173260	0.000000
O	1.307370	1.113560	0.000000
H	3.132600	0.122140	0.000000
H	1.683500	-2.186300	0.000000
O	-1.307370	-1.113560	0.000000
C	0.025070	0.681740	0.000000
C	-0.025070	-0.681740	0.000000
C	-1.307370	1.173260	0.000000
H	-1.683500	2.186300	0.000000
C	-2.063090	0.032500	0.000000
H	-3.132600	-0.122140	0.000000

Cartesian coordinates (Å) of excited state (S_1) optimized geometries

Thiophene – minimum a (PBE0)

C	0.010663	-1.269595	0.532071
C	-1.230376	-0.691025	0.097647
C	-1.279410	0.744060	0.141827
C	-0.041478	1.293957	0.133706
S	1.004383	-0.088227	-0.314169
H	0.264323	-2.296128	0.288706
H	-2.053139	-1.301379	-0.261655
H	-2.206190	1.301416	0.208362
H	0.324205	2.299268	0.248728

Thiophene – minimum a (M06-2X)

C	0.013182	-1.264190	0.510757
C	-1.242668	-0.687842	0.096731
C	-1.283649	0.745523	0.146104
C	-0.043639	1.288393	0.129884
S	1.012141	-0.092366	-0.308335
H	0.273082	-2.294284	0.309485
H	-2.053444	-1.301334	-0.276046
H	-2.204609	1.306522	0.224247
H	0.322586	2.291926	0.242395

Thiophene – minimum a (ADC(2))

C	-0.074058	-1.381002	-0.007198
C	-1.297082	-0.782362	-0.408073
C	-1.297163	0.639367	-0.406884
C	-0.074203	1.237469	-0.005019
S	1.041518	-0.071278	-0.522578
H	0.234415	-2.377430	-0.289742
H	-2.172849	-1.366304	-0.656879
H	-2.173002	1.223624	-0.654699
H	0.234167	2.234402	-0.285893

Thiophene – minimum b (PBE0)

C	0.012978	-1.191234	0.277179
C	-1.334586	-0.683180	0.247457
C	-1.336292	0.677982	0.144134
C	0.010297	1.187747	0.097792
S	1.149397	-0.042480	-0.371178
H	0.347218	-1.996033	0.928848
H	-2.204128	-1.308855	0.399287
H	-2.207341	1.317297	0.199600
H	0.342995	2.080428	0.623619

Thiophene – minimum b (M06-2X)

C	0.014340	-1.187930	0.278069
C	-1.337857	-0.682739	0.240853
C	-1.339179	0.676230	0.139026
C	0.011997	1.183998	0.100194
S	1.140253	-0.045277	-0.405405
H	0.354739	-1.966401	0.953681
H	-2.205837	-1.307015	0.393384
H	-2.208462	1.314533	0.196489
H	0.350544	2.056275	0.650446

Thienothiophene (PBE0)

C	-5.457002	-0.359618	0.239649
C	-5.056477	-1.665316	-0.101888
C	-3.869158	-2.015327	0.501539
S	-4.370763	0.437606	1.325997
C	-3.234224	-0.904044	1.169991
C	-1.862397	-1.018252	1.206399
C	-1.425696	-2.277874	0.754240
S	-2.716094	-3.336082	0.295430
H	-6.349812	0.144334	-0.097994
H	-5.628963	-2.290998	-0.772007
H	-1.176168	-0.246945	1.526419
H	-0.402215	-2.614734	0.690282

Thienothiophene (M06-2X)

C	-5.411601	-0.353279	0.219944
C	-5.028541	-1.666054	-0.089079
C	-3.908375	-2.066856	0.610728
S	-4.400355	0.403168	1.410115
C	-3.267894	-0.945517	1.285009
C	-1.892276	-1.019981	1.199686
C	-1.452252	-2.259994	0.715677
S	-2.741525	-3.371615	0.379657
H	-6.250007	0.179647	-0.198371
H	-5.557342	-2.270379	-0.810417
H	-1.211767	-0.221840	1.454692
H	-0.427035	-2.554550	0.560418

Thienothiophene (ADC(2))

C	-0.506077	0.293742	0.222888
C	-0.311251	-0.037682	1.561718
S	0.173686	1.821769	-0.173205
C	0.953022	1.991660	1.442518
C	0.365146	0.955951	2.322329
C	2.373947	1.968951	1.504186
S	1.662211	0.419117	3.452030
C	2.894362	1.193094	2.537373
H	-0.651005	-0.978717	1.973721
H	-1.093591	-0.253860	-0.498181
H	3.928860	1.130558	2.838847
H	3.011743	2.503112	0.812369

Dithienothiophene (PBE0)

C	9.919322	12.150933	0.548947
C	8.613947	12.637574	0.618574
C	7.708159	11.635326	0.903303
C	8.321170	10.347080	1.056832
H	8.370880	13.679100	0.464097
C	7.419676	9.359468	1.337155
C	6.069950	9.840641	1.412303
C	5.153723	8.846714	1.692861
C	5.767778	7.602771	1.838164
H	4.086768	8.985551	1.793537
S	10.053684	10.446276	0.833233
H	10.811692	12.721265	0.342798
S	5.964318	11.571832	1.121943
S	7.488426	7.635916	1.630311
H	5.283055	6.664641	2.059649

Dithienothiophene (M06-2X)

C	9.912828	12.140944	0.511327
C	8.611638	12.631334	0.594818
C	7.711997	11.648457	0.956839
C	8.328122	10.358364	1.128982
H	8.365337	13.663578	0.400179
C	7.429366	9.373823	1.409215
C	6.072425	9.852296	1.467097
C	5.152993	8.842210	1.668876
C	5.766366	7.598269	1.799260
H	4.083663	8.972779	1.728551
S	10.057010	10.445965	0.860351
H	10.798287	12.704134	0.268304
S	5.968303	11.596001	1.219499
S	7.496568	7.641117	1.658883
H	5.277649	6.655819	1.981525

Dithienothiophene (ADC(2))

C	9.882434	12.090064	0.412217
C	8.579453	12.601728	0.531794
C	7.718954	11.688157	1.113071
C	8.352887	10.396913	1.336174
H	8.318913	13.602956	0.222714
C	7.451742	9.409670	1.616128
C	6.077633	9.890029	1.622858
C	5.160007	8.855591	1.593710
C	5.784114	7.600188	1.684976
H	4.087567	8.967344	1.536692
S	10.053753	10.444150	0.944235
H	10.753501	12.622007	0.062903
S	5.996567	11.645928	1.487006
S	7.520371	7.668728	1.731129
H	5.294654	6.641637	1.758099

Bithiophene (PBE0)

C	-5.041520	-0.026361	0.102854
C	-4.865713	-1.396231	-0.052575
C	-3.546582	-1.800082	0.046828
C	-2.664110	-0.712243	0.286875
S	-3.567007	0.808038	0.378767
H	-5.970451	0.521401	0.066595
H	-5.694436	-2.067276	-0.233439
H	-3.195840	-2.818950	-0.042748
C	-1.292272	-0.720194	0.440770
C	-0.409454	0.367625	0.679882
C	0.909987	-0.036009	0.775633
C	1.085648	-1.405884	0.619181
S	-0.389387	-2.240352	0.346633
H	-0.760204	1.386284	0.771411
H	1.739036	0.635038	0.954773
H	2.014743	-1.953472	0.653079

Bithiophene (M06-2X)

C	-5.037451	-0.026127	0.104486
C	-4.863456	-1.396203	-0.051383
C	-3.544795	-1.803472	0.045637
C	-2.661195	-0.712024	0.285627
S	-3.563958	0.810846	0.379012
H	-5.966275	0.518344	0.068603
H	-5.692621	-2.063957	-0.231077
H	-3.193206	-2.820334	-0.045321
C	-1.294752	-0.720314	0.438707
C	-0.411152	0.371135	0.678695
C	0.907511	-0.036129	0.775691
C	1.081509	-1.406203	0.619811
S	-0.391985	-2.243179	0.345302
H	-0.762746	1.387994	0.769674
H	1.736676	0.631627	0.955380
H	2.010336	-1.950671	0.655677

Bithiophene (ADC(2))

C	-5.040262	-0.020099	0.105360
C	-4.866963	-1.405869	-0.053067
C	-3.551244	-1.820214	0.042092
C	-2.660928	-0.720207	0.283887
S	-3.560675	0.805313	0.378225
H	-5.967930	0.528507	0.071151
H	-5.703111	-2.066219	-0.232233
H	-3.198618	-2.837224	-0.048969
C	-1.294919	-0.711970	0.439512
C	-0.404585	0.388010	0.681357
C	0.910993	-0.026516	0.777689
C	1.084189	-1.412372	0.619896
S	-0.395316	-2.237641	0.346176
H	-0.757065	1.405165	0.771353
H	1.747123	0.633777	0.957148
H	2.011750	-1.961106	0.654944

Excitation energies and spectrum of terthiophene.

Table S3. Excitation energies (in eV) and oscillator strengths (in parenthesis) of the two lowest bright states of terthiophene. Values are computed with the cc-pVQZ basis set.

	terthiophene	
	A''	A'
PBE0	3.36 (0.740)	5.02 (0.080)
M06-2X	3.60 (0.730)	5.41 (0.136)
CIS	3.95 (0.883)	6.39 (0.130)
CIS(D)	3.99 (-)	5.59 (-)
ADC2	3.75 (0.878)	5.36 (0.154)
D ₁	0.035	
%doubles	10.5	10.7

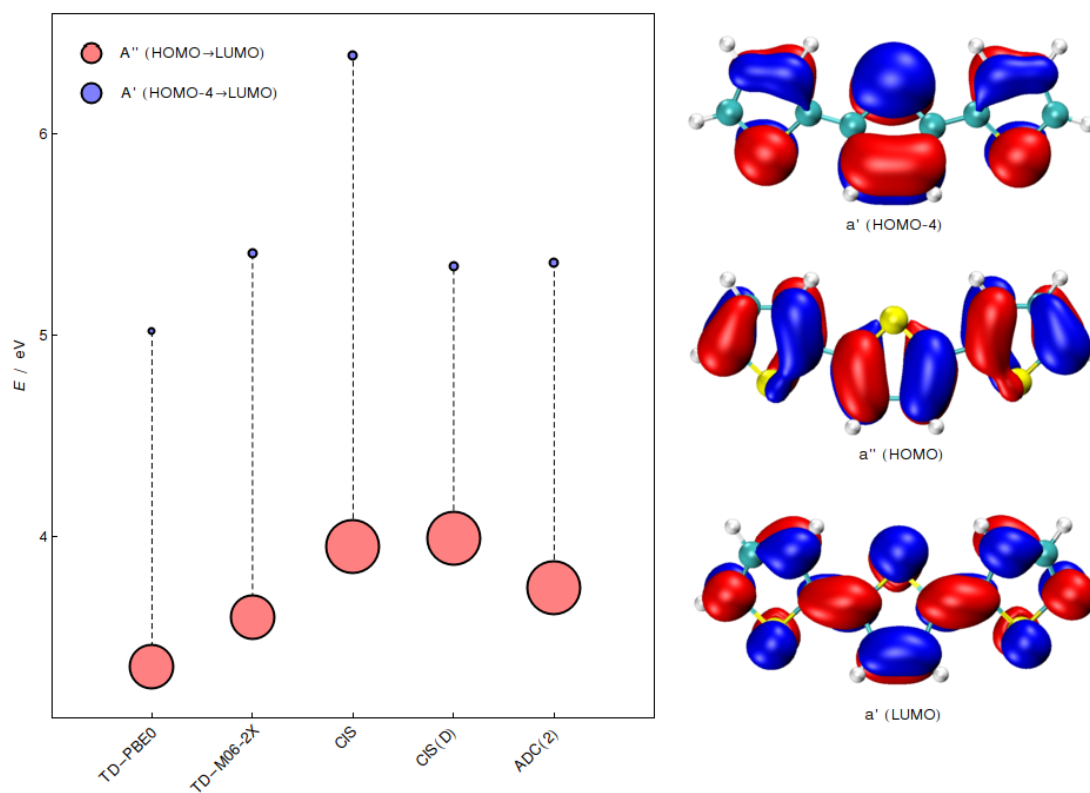


Figure S6. Excitation energies of the two lowest bright $\pi\pi^*$ states of terthiophene. Radii of the circles are proportional to the oscillator strengths while colors denote character. Numerical values are taken from table S3.

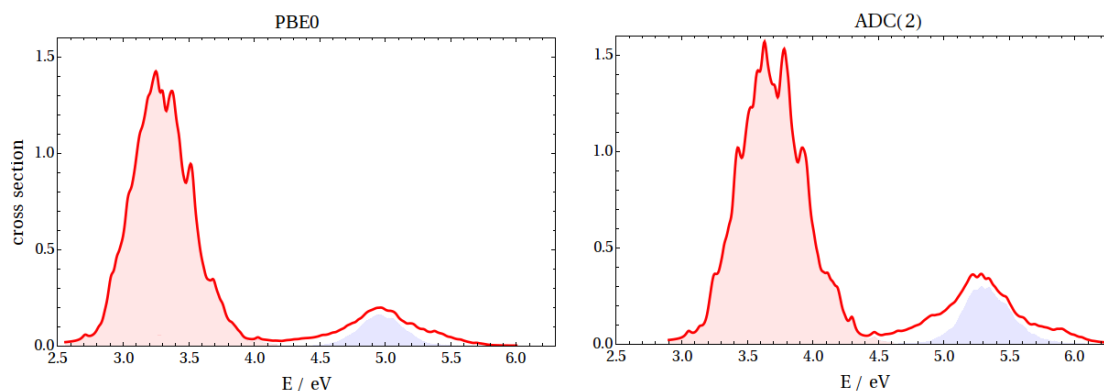


Figure S7. Photoabsorption spectra computed from Wigner distribution (red line) of terthiophene (second row). The spectra were decomposed into contributions from S_1 and $S_6+S_7+S_8$. The states represented by the red-shaded areas have a dominant HOMO \rightarrow LUMO character, while states depicted as blue are dominated by HOMO-4 \rightarrow LUMO excitations. The cc-pVTZ basis set was used.

Excited state geometries of bithiophene.

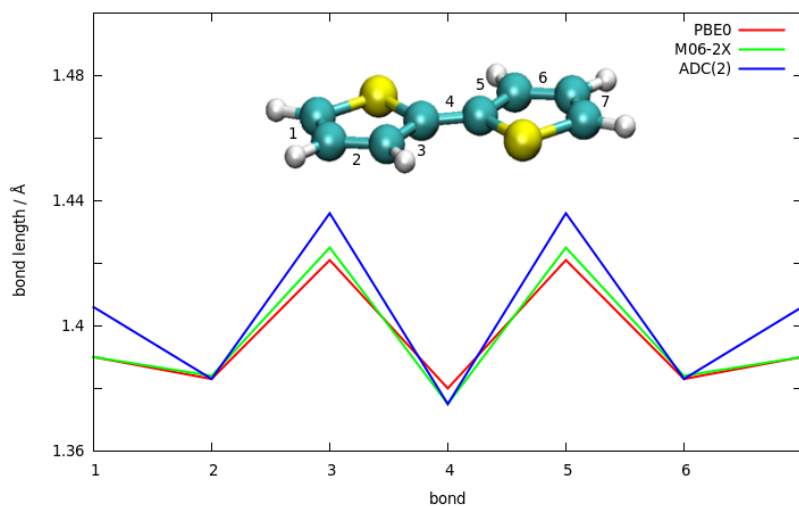


Figure S8. CC bond length alternations of the planar S_1 minimum of bithiophene. The cc-pVTZ basis set was used.

Excitation energies of furan and furofuran.

Table S4. Excitation energies (in eV) and oscillator strengths (in parenthesis) of furan and furofuran. Values are computed with the cc-pVQZ basis set.

	furan		furofuran	
	B ₂	A ₁	B _u (H-L)	B _u (H-1-L)
PBE0	6.28 (0.155)	6.88 (0)	5.27 (0.354)	6.39 (0.039)
M06-2X	6.39 (0.161)	7.15 (0)	5.43 (0.366)	6.71 (0.056)
CIS	6.56 (0.203)	8.15 (0.006)	5.67 (0.507)	7.92 (0.075)
CIS(D)	6.82 (-)	6.87 (-)	5.87 (-)	6.38 (-)
ADC2	6.67 (0.188)	6.83 (0.002)	5.63 (0.410)	6.36 (0.098)
D ₁	0.034		0.037	
%doubles	6.37	10.38	8.32	11.03

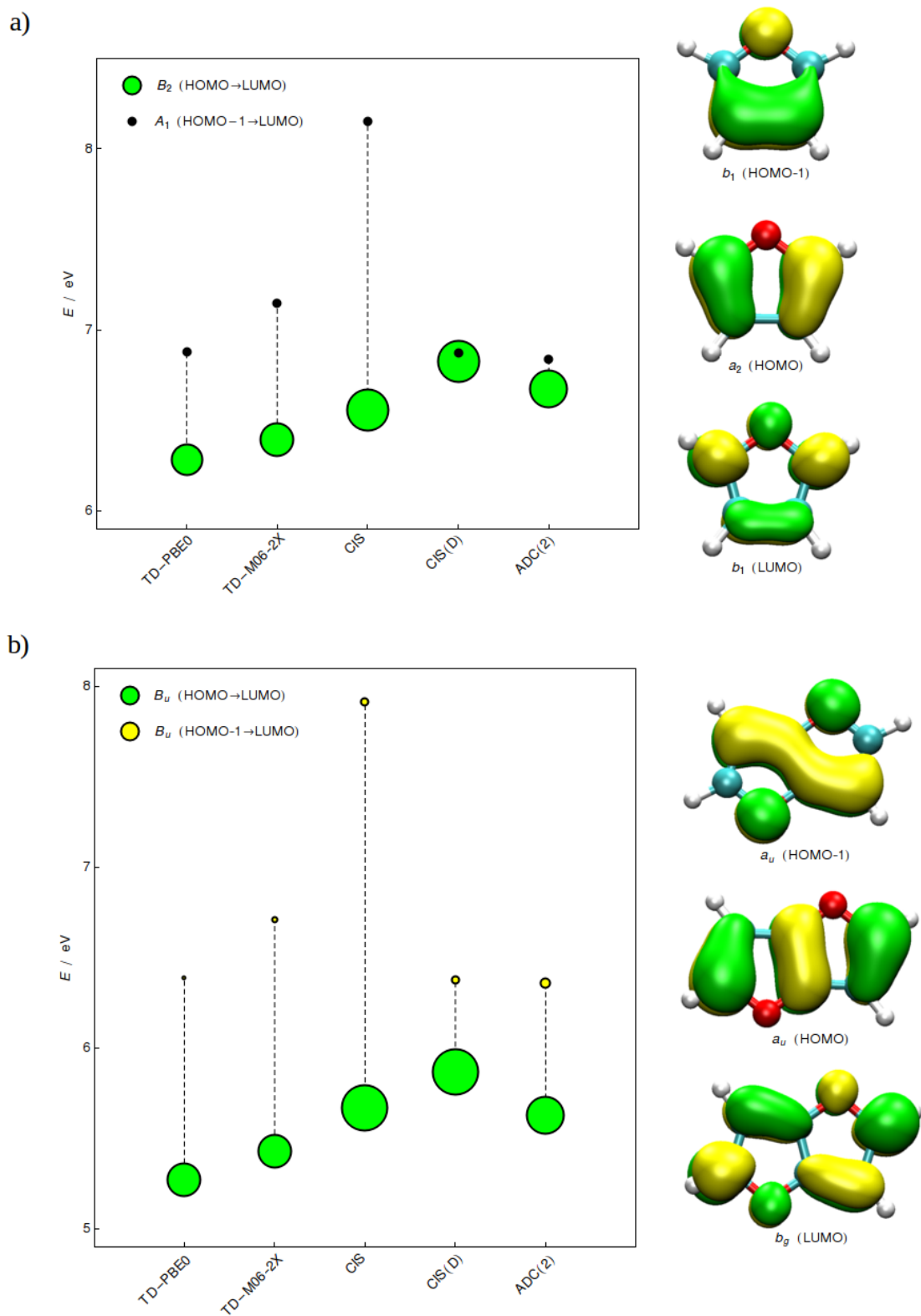


Figure S9. Excitation energies of the two lowest bright $\pi\pi^*$ states of: a) furan and b) furofuran. Radii of the circles are proportional to the oscillator strengths while colors denote character. The states depicted in black have an oscillator strength close to zero.

Numerical values are taken from Table S4.

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