Electronic Supplementary Information (ESI): First Principles Study of Photo-oxidation Degradation Mechanisms in P3HT for Organic Solar Cells

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1 Basis set convergence and comparison between VASP and G09

Table S1 Binding energies and optimized S−O distances of ethylthiophene-SOH calculated using PBE0 with different basis sets as implemented in Gaussian 09. All calculations included a dielectric solvent of $\varepsilon = 3$.

Basis set	6-311g**	aug-cc-pvdz	aug-cc-pvtz	aug-cc-pvqz
d_{S-O} (Å)	2.38	2.32	2.24	2.20
E_b (eV)	−0.218	−0.22	−0.208	−0.214

Table S2 Binding energies and optimized S−O and S−H distances of ethylthiophene-SOH (without solvent) calculated using PBE0/plane-wave PAW (VASP) and PBE0/aug-cc-pvdz (G09).

Method	d_{S-O} (Å)	d_{S-H} (Å)	E_b (eV)
VASP	2.18	2.52	−0.25
G09	2.34	2.59	−0.22

2 MP2 optimized geometry

Table S3 Binding energies and optimized S−O and S−H distances of ethylthiophene-SOH calculated using HF and MP2. *E*//MP2 denotes the single point reaction energy calculated at fixed MP2 geometry. All calculations used the aug-cc-pvdz basis set and a dielectric solvent field of $\varepsilon = 3$.

Method	d_{S-O} (Å)	d_{S-H} (Å)	E_b (eV)
HF	4.01	3.11	−0.08
MP2	3.71	2.95	−0.22
CCSD(T)//MP2			−0.18

3 Transition barrier between the SOH and COH complexes

Fig. S2 shows the transition state and energy profile between SOH and the $C^{(2)}OH$ complex which lies −0.95 and −1.12 eV below SOH, respectively, calculated using PBE/6-31+G(d,p) and PBE0/6-31+G(d,p). With a dielectric continuum ($\varepsilon = 3$) and thermal correction included, we found a reaction barrier of 0.13 eV with PBE and −0.07 eV with PBE0, indicating that the SOH can relax into the COH configuration without overcoming a significant activation barrier.

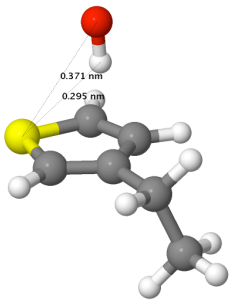

Figure S1 Geometry optimization using the MP2 theory yields a "H-down" geometry in which H is closer to S than O.

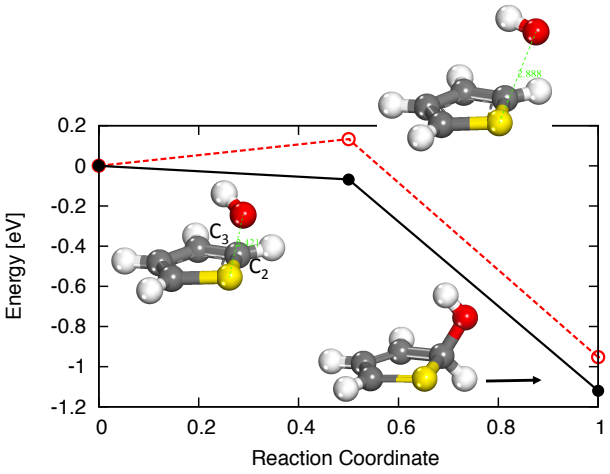

Figure S2 Potential energy profile for the thiophene-OH complexes calculated using PBE/6-31+G(d,p) (open circle) and PBE0/6-31+G(d,p) (filled circle). The energy is the same if calculated with the aug-cc-pvdz basis set.

4 The second reaction pathway between COH and O_2

Fig. S3 shows the energy profile for the $2+4$ cycloaddition reaction between the $C^{(3)}OH$ complex and an O_2 triplet. In the transition state, the two O atoms of an O_2 triplet add to $C^{(2)}$ and $C^{(5)}$ of COH and form a C−O−O−C bridge. In the final product, the O−O bond breaks, leaving an oxidized thiophene on the carbon site.

5 Influence of the simulation cell size on the reaction barriers in P3HT

The minimum energy paths for the ROO· attack on sulfur of P3HT calculated for a unit cell of P3BT and a supercell that doubles the P3BT unit cell along the backbone direction. By doubling the unit cell, the reaction energy shifts down from -0.6 to -0.89 eV, and the reaction barrier shifts down from 0.85 to 0.6 eV.

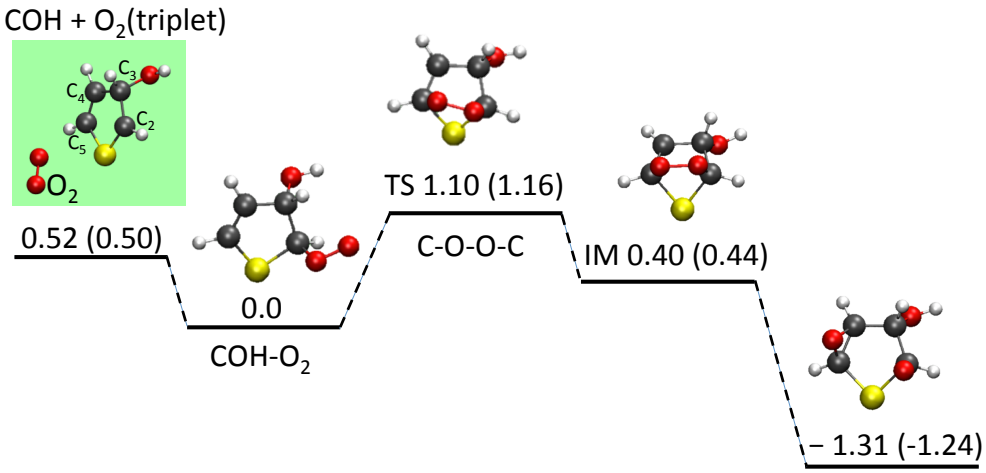

Figure S3 Energy profile for the $2+4$ cycloaddition reaction between the $C^{(3)}OH$ complex and an O2 triplet calculated using PBE0/6-31+G(d,p). TS is the transition state forming the C-O-O-C bridge. IM is the intermediate state. A thermal correction and dielectric solvent of $\varepsilon = 3$ were applied ($\varepsilon = 1$ results are shown in parenthesis). Energies are in eV.

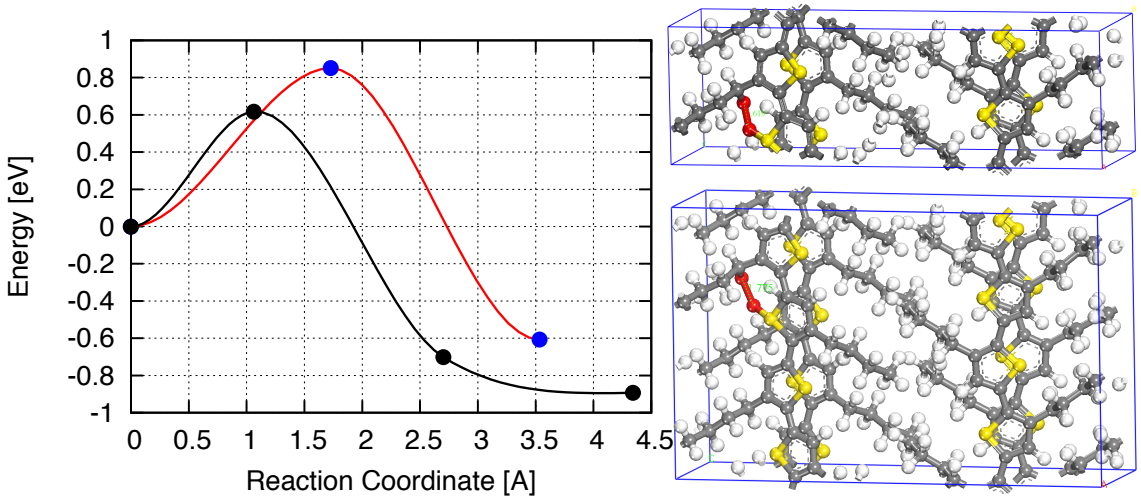

Figure S4 Minimum energy path for the alkylperoxyl (ROO·) + thiophene reaction in P3HT calculated using the NEB method and the PBE functional for a P3BT unit cell (red line) and a doubled unit cell along the backbone direction (black line).

atom	*x*	*y*	*z*
TOH vDW complex, PBE/6-31+G(d,p) Fig. S2 -628.295554			
S	-0.623799	-0.000898	-0.685811
C	0.475066	-1.253916	-0.166531
C	0.473918	1.253712	-0.167863
C	1.621506	-0.720953	0.375702
C	1.620835	0.722392	0.374945
H	2.445336	-1.329666	0.757277
H	2.444081	1.332275	0.755907
H	0.194432	-2.299303	-0.295927
H	0.192311	2.298699	-0.298381
O	-2.328691	0.000380	0.745974
H	-1.813789	0.001917	1.588788
TOH covalent complex, PBE/6-31+G(d,p) Fig. S2 -628.336396			
S	0.382685	-1.251593	0.100041
C	1.604864	-0.057490	-0.246729
C	-0.929682	0.089670	0.420786
C	1.148547	1.266163	-0.106838
C	-0.181353	1.383443	0.270349
H	1.803552	2.123732	-0.289821
H	-0.709172	2.327250	0.433018
H	2.605190	-0.373631	-0.547969
H	-1.316744	-0.093372	1.437877
O	-2.069520	-0.037132	-0.417353
H	-1.803890	0.247847	-1.320348
TOH TST, PBE/6-31+G(d,p) Fig. S2 -628.291468			
S	0.338465	-0.941524	-0.430812
C	-1.156838	-0.942195	0.411424
C	0.230026	0.788019	-0.731025
C	-1.715289	0.332796	0.478094
C	-0.923187	1.317993	-0.179797
H	-2.667246	0.539553	0.974225
H	-1.191645	2.374358	-0.256665
H	-1.539562	-1.865264	0.848563
H	0.995742	1.276130	-1.330755
O	2.318290	0.368687	0.672024
H	1.832692	0.810435	1.409269

Table S4 Cartesian coordinates, in Å, for molecules and complexes. The species, DFT or quantum chemistry method used for geometry optimization, basis set, appearance in the text or supporting section, and energy in Hartree. T and ET stand for thiophene and ethylthiophene, respectively. In all cases, the PCM dielectric solvation option is applied with ε_o=3 unless otherwise noted. Gas phase geometries are almost identical to those computed using the PCM solvation option and are not listed.

atom	*x*	*y*	*z*
TOH vDW complex, PBE0/6-31+G(d,p) Fig. S2 -628.333999			
S	-0.567281	-0.001275	-0.740416
C	0.489936	-1.241449	-0.167780
C	0.488360	1.241174	-0.169747
C	1.600652	-0.715718	0.424641
C	1.599737	0.717810	0.423508
H	2.396073	-1.321251	0.846246
H	2.394365	1.325026	0.844184
H	0.224500	-2.281724	-0.305861
H	0.221550	2.280883	-0.309440
O	-2.421616	0.000628	0.767765
H	-1.859180	0.001544	1.565677
TOH covalent complex, PBE0/6-31+G(d,p) Fig. S2 -628.382184			
S	0.336720	-1.244741	0.100679
C	1.591952	-0.096139	-0.242070
C	-0.914440	0.104880	0.416446
C	1.175549	1.230928	-0.108025
C	-0.142357	1.379346	0.263252
H	1.847572	2.064875	-0.288807
H	-0.646594	2.327846	0.418654
H	2.577415	-0.439346	-0.532630
H	-1.301116	-0.046019	1.429361
O	-2.044379	0.008877	-0.412023
H	-1.773981	0.223398	-1.318876
TOH TST, PBE0/6-31+G(d,p) Fig. S2 -628.328327			
S	-0.295149	-0.029492	0.724316
C	0.761038	-1.238402	0.096294
C	0.710700	1.238825	0.131069
C	1.839930	-0.681338	-0.533025
C	1.811342	0.745637	-0.512350
H	2.628363	-1.267092	-0.994145
H	2.576929	1.376219	-0.952186
H	0.532342	-2.287600	0.235302
H	0.430429	2.270685	0.301300
O	-3.667730	0.052865	-0.560930
H	-2.841905	-0.431596	-0.783818

Table S5 Same as previous table.

atom	*x*	*y*	*z*
O_2 radical, PBE0/6-31+G(d,p) Fig. 3 and Fig. S3, -150.174398			
O	0.0000	0.0000	0.6014
O	0.0000	0.0000	-0.6014
TOH radical, PBE0/6-31+G(d,p) Fig. 3 and S3, -628.371028			
S	-1.524171	-0.453455	-0.144719
C	0.005804	-1.089133	0.318769
C	-0.892507	1.188993	-0.088884
C	1.087429	-0.059940	0.430336
C	0.406571	1.261439	0.222890
H	1.563917	-0.107711	1.424617
H	0.957953	2.192933	0.290516
H	0.146403	-2.157116	0.425933
H	-1.563479	2.012586	-0.302311
O	2.121571	-0.192462	-0.561609
H	2.665595	-0.953864	-0.329052
TOH radical bound to O_2, PBE0/6-31+G(d,p) Fig. 3 and Fig. S3, -778.587577			
S	-0.915238	-1.332402	-0.527308
C	0.497892	-0.220522	-0.447805
C	-1.797899	-0.323979	0.620422
C	0.052390	1.121519	0.183611
C	-1.226056	0.845531	0.913926
H	0.854367	1.441016	0.863265
H	-1.659660	1.578798	1.584608
H	0.969479	-0.089474	-1.423388
H	-2.742356	-0.695196	1.002777
O	-0.189419	2.111153	-0.795486
H	0.651417	2.505447	-1.055856
O	1.485067	-0.865213	0.420569
O	2.630927	-0.240622	0.355491

Table S6 Same as previous table.

atom	*x*	*y*	*z*
O_2-TOH radical (S-O bond broken), PBE0/ 6-31+G(d,p), Fig. 3, -778.660326			
S	1.986158	-0.331615	-0.405690
C	-1.877737	-0.979810	0.191936
C	1.072756	0.585954	0.766382
C	-1.196709	0.274385	-0.337920
C	-0.254609	0.804016	0.706621
H	-0.633314	-0.042227	-1.234150
H	-0.723561	1.408984	1.479972
H	-1.224634	-1.814819	0.500075
H	1.685403	0.996405	1.566946
O	-2.149498	1.236488	-0.678861
H	-3.020313	0.829960	-0.528249
O	-3.084247	-1.043002	0.262799
O	3.443205	-0.215952	0.009104
O_2-TOH radical (TST), PBE0/6-31+G(d,p) Fig. 3, -778.532866			
S	-1.278444	0.607257	-0.488778
C	0.095873	-0.816354	-0.450291
C	-0.114064	1.737615	0.142883
C	1.294195	-0.232543	0.320498
C	1.084456	1.242124	0.488643
H	1.310678	-0.715825	1.310031
H	1.893188	1.858387	0.869460
H	0.371714	-1.154207	-1.454965
H	-0.426598	2.771681	0.242323
O	2.520509	-0.432897	-0.354735
H	2.816073	-1.337558	-0.204080
O	-0.682849	-1.714174	0.232319
O	-1.796748	-0.693384	0.628326
TOH radical O_2 bridge, PBE0/6-31+G(d,p) Fig. S3, -778.574433			
S	-0.572570	1.419298	-0.051691
C	0.157363	0.026940	-0.990376
C	-0.899432	-0.063198	1.008362
C	1.215043	-0.584648	-0.043756
C	0.468129	-0.574683	1.250943
H	1.430370	-1.609504	-0.384405
H	0.900050	-0.775734	2.223094
H	0.491538	0.291971	-1.994739
H	-1.547866	0.129223	1.862457
O	2.404745	0.170024	0.044462
H	2.999551	-0.105164	-0.662425
O	-0.891805	-0.912049	-1.132531
O	-1.607833	-0.941229	0.142074

Table S7 Same as previous table.

atom	x	y	z
O_2-TOH radical TST, PBE0/6-31+G(d,p) Fig. S3, -778.547816			
S	-0.631871	1.408208	-0.248635
C	0.085846	-0.110038	-0.998186
C	-0.649797	0.411591	1.189353
C	1.167560	-0.579311	0.002781
C	0.478953	-0.395459	1.320245
H	1.366047	-1.643346	-0.186670
H	0.699484	-0.984817	2.201888
H	0.424609	0.043679	-2.024229
H	-1.337442	0.645891	1.995066
O	2.353817	0.182476	-0.056313
H	2.886044	-0.127185	-0.798023
O	-0.956462	-1.047386	-1.024126
O	-1.450377	-1.188371	0.293559
O_2-TOH radical (O_2 separated), PBE0/ 6-31+G(d,p) Fig. S3, -778.637722			
S	-1.264921	-0.466980	-0.816695
C	0.161027	-1.178863	0.152846
C	-0.786969	1.208591	-0.381901
C	1.225732	-0.063143	0.301968
C	0.556244	1.285964	0.185684
H	1.694169	-0.180946	1.288097
H	1.194635	2.158316	0.061227
H	0.562626	-2.036038	-0.410578
H	-1.256293	1.984682	-0.981944
O	2.170034	-0.116898	-0.742584
H	2.838625	-0.779009	-0.537582
O	-0.527245	-1.496003	1.261657
O	-0.609192	1.464074	0.992967

Table S8 Same as previous table.

atom	x	y	z
ETOH radical, PBE/aug-cc-pvdz Table. 1,-706.877			
S	-1.66044	0.06922	-0.57646
C	-0.08779	-0.58051	-0.96046
C	-0.94660	1.35684	0.37767
C	0.93544	0.14658	-0.38253
C	0.42251	1.26390	0.38924
C	2.40079	-0.17115	-0.52692
H	1.06367	1.97537	0.92479
C	3.07070	-0.55825	0.80323
H	2.92024	0.71308	-0.95032
H	2.52182	-0.99234	-1.25811
H	3.00447	0.25875	1.54623
H	4.14226	-0.78122	0.64327
H	-1.86270	-1.14367	1.62357
O	-2.62080	-1.13044	0.99782
H	-0.02048	-1.46957	-1.59564
H	-1.60177	2.08665	0.86330
H	2.59567	-1.45551	1.24242
ETOH radical, PBE0/aug-cc-pvdz Table. 1, -706.933			
S	-1.519960	0.006311	-0.754362
C	-0.073186	-0.900519	-0.468331
C	-0.849936	1.410825	0.010348
C	0.881250	-0.162582	0.176686
C	0.418435	1.176362	0.447265
C	2.247459	-0.661025	0.543656
H	1.019075	1.929795	0.956436
C	3.366639	0.023011	-0.240027
H	2.289726	-1.746370	0.379490
H	2.407483	-0.496522	1.620858
H	3.263059	-0.160708	-1.318364
H	4.347309	-0.357047	0.077755
H	-2.421593	-0.583502	1.575412
O	-3.053437	-0.686891	0.843911
H	-0.018488	-1.935651	-0.797132
H	-1.445294	2.317192	0.088818
H	3.361603	1.110539	-0.082353
ET, PBE0/aug-cc-pvdz Table. 1, -631.254			
S	2.009770	-0.436083	0.184818
C	0.430381	-1.085551	-0.080556
C	1.424977	1.178747	0.011991
C	-0.506915	-0.107099	-0.292588
C	0.080716	1.198568	-0.236545
C	-1.967078	-0.364424	-0.535039
H	-0.480004	2.121828	-0.382748
C	-2.861477	0.112876	0.607528
H	-2.118573	-1.441101	-0.695253
H	-2.271196	0.137519	-1.466921
H	-2.609455	-0.400448	1.545967
H	-3.918543	-0.087604	0.382851
H	0.280508	-2.162951	-0.067692
H	2.111045	2.018189	0.099803
H	-2.753729	1.193187	0.778158

Table S9 Same as previous table.

atom	x	y	z
ETOH radical, PBE0-D3BJ/aug-cc-pvdz Table. 1, -706.948			
S	-1.52350	0.00423	-0.76600
C	-0.07558	-0.90108	-0.48177
C	-0.85813	1.40567	0.00944
C	0.87364	-0.16609	0.17364
C	0.40833	1.17048	0.45128
C	2.23905	-0.66250	0.54064
H	1.00580	1.92046	0.96873
C	3.35268	0.03711	-0.23586
H	2.28683	-1.74569	0.36540
H	2.39564	-0.50697	1.61949
H	3.24743	-0.13573	-1.31572
H	4.33649	-0.33884	0.07644
H	-2.35494	-0.55486	1.58495
O	-3.00579	-0.68824	0.87539
H	-0.01698	-1.93382	-0.81657
H	-1.45633	2.30953	0.09238
H	3.33851	1.12270	-0.06644
ETOH radical, PBE-D3BJ/aug-cc-pvdz Table. 1, -706.895			
S	-1.55241	-0.04263	-0.71913
C	-0.08277	-0.93561	-0.42325
C	-0.86152	1.41436	-0.03022
C	0.88575	-0.16144	0.18463
C	0.42280	1.19647	0.40257
C	2.26290	-0.64186	0.55322
H	1.03567	1.97669	0.87070
C	3.37479	0.03457	-0.26553
H	2.31293	-1.73852	0.41996
H	2.43301	-0.44082	1.63090
H	3.25671	-0.17828	-1.34437
H	4.36814	-0.33334	0.05222
H	-2.40692	-0.50802	1.59507
O	-3.00384	-0.62501	0.82279
H	-0.03531	-1.99082	-0.70971
H	-1.46865	2.32360	0.01420
H	3.36194	1.13274	-0.13369

Table S10 Same as previous table.

atom	x	y	z
ETOH radical, PBE0/aug-cc-pvtz Table. S1, -706.019			
S	-1.51513	-0.00789	-0.72608
C	-0.07668	-0.90094	-0.43547
C	-0.85136	1.40500	-0.00158
C	0.87529	-0.15313	0.18779
C	0.41292	1.18425	0.43306
C	2.24117	-0.63960	0.55489
H	1.01219	1.94291	0.92041
C	3.34915	0.00899	-0.26842
H	2.27974	-1.72452	0.43630
H	2.41595	-0.43363	1.61611
H	3.23398	-0.21838	-1.33037
H	4.32829	-0.35425	0.05116
H	-2.43101	-0.57043	1.55722
O	-3.02273	-0.67614	0.79798
H	-0.01988	-1.93479	-0.74208
H	-1.44312	2.30541	0.06166
H	3.34492	1.09566	-0.15855
ETOH radical, PBE0/aug-cc-pvqz Table. S1, -706.045			
S	-1.51733	-0.01663	-0.71462
C	-0.08040	-0.90354	-0.42314
C	-0.85654	1.40218	-0.00897
C	0.87310	-0.14949	0.19160
C	0.40955	1.18883	0.42581
C	2.24062	-0.63079	0.55819
H	1.00856	1.95278	0.90438
C	3.34397	0.00691	-0.27934
H	2.27886	-1.71683	0.45418
H	2.42053	-0.41092	1.61535
H	3.22333	-0.23436	-1.33714
H	4.32466	-0.35145	0.03954
H	-2.42019	-0.56818	1.55151
O	-3.00104	-0.66832	0.78489
H	-0.02238	-1.93953	-0.72115
H	-1.44951	2.30193	0.04740
H	3.33990	1.09454	-0.18426

Table S11 Same as previous table.

atom	x	y	z
ETOH radical, MP2/aug-cc-pvdz Table. S3, -705.972			
S	1.745323	-0.987245	-0.409823
C	0.232063	-0.462481	-1.071040
C	1.254552	-0.562879	1.195692
C	-0.636707	0.016531	-0.088933
C	-0.038704	-0.046935	1.212728
C	-2.039475	0.504344	-0.357119
H	-0.530670	0.285410	2.131258
C	-3.092243	-0.505005	0.129543
H	-2.162155	0.681573	-1.438436
H	-2.190930	1.472727	0.149977
H	-2.971459	-1.470119	-0.388494
H	-4.111704	-0.133325	-0.063313
H	0.877830	1.795364	0.045925
O	1.260791	2.678925	-0.137897
H	0.054651	-0.530735	-2.146310
H	1.938883	-0.712064	2.032478
H	-2.992862	-0.685759	1.212036
ET, MP2/aug-cc-pvdz Table. S3, -630.408			
S	2.006371	-0.454469	0.189139
C	0.420471	-1.087756	-0.107110
C	1.444371	1.177054	0.031154
C	-0.517828	-0.080154	-0.321836
C	0.081603	1.218524	-0.239852
C	-1.987695	-0.326122	-0.563571
H	-0.463557	2.156435	-0.379881
C	-2.842067	0.078489	0.649310
H	-2.144894	-1.394117	-0.789403
H	-2.313561	0.243756	-1.451067
H	-2.547893	-0.499163	1.540583
H	-3.911940	-0.104144	0.455951
H	0.257149	-2.167341	-0.112020
H	2.143854	2.007688	0.139911
H	-2.714220	1.148183	0.881135

Table S12 Same as previous table. See Fig. S1 for the schematic illustration of the ETOH structure.

atom	x	y	z
ETOH radical, PBE0/aug-cc-pvdz (no solvation), Table. S2, -706.922			
S	-1.50427	-0.06175	-0.74964
C	-0.04959	-0.93419	-0.41578
C	-0.84920	1.38389	-0.05748
C	0.89771	-0.15605	0.19370
C	0.42116	1.18699	0.39520
C	2.26929	-0.62236	0.58337
H	1.01080	1.97084	0.86964
C	3.37905	0.02946	-0.24181
H	2.32147	-1.71461	0.47680
H	2.43202	-0.40353	1.65052
H	3.25864	-0.20040	-1.30882
H	4.36532	-0.33195	0.07859
H	-2.52737	-0.49201	1.58996
O	-3.14198	-0.57369	0.84219
H	0.02097	-1.98321	-0.69064
H	-1.45695	2.28341	-0.02003
H	3.36876	1.12243	-0.13265
ETOH radical, PBE0/VASP (no solvation), Table. S2			
S	5.49332	6.91913	7.31950
C	6.93614	6.06632	7.60802
C	6.14159	8.36209	7.96256
C	7.89426	6.84556	8.19261
C	7.41865	8.18264	8.39008
C	9.26463	6.38398	8.57367
C	10.37481	7.03362	7.75416
H	8.01144	8.96978	8.84090
H	9.31651	5.29630	8.47331
H	9.42468	6.60428	9.63605
H	10.26056	6.80550	6.69174
H	11.35460	6.67391	8.07738
H	4.47083	6.51798	9.57954
H	7.00923	5.02402	7.33309
H	5.53817	9.25689	7.99785
H	10.36529	8.12120	7.86324
O	3.94104	6.44005	8.76942

Table S13 Same as previous table.