Supporting Information

Four-electron oxygen reduction by Tetrathiafulvalene

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Figure S1. Cyclic voltammogram at Pt microelecrode in the bulk of an organic solution containing 5mm TTF and 5mM BATB. Using Ag/AgCl as the reference electrode and Pt as the counterelectrode.

Figure S2. UV-visible spectra of the organic phase after biphasic reaction between 1 mM TTF and 10 mM H_2O_2 under anaerobic conditions (cell II, Scheme 1: TTF=1mM, pH=2).

Figure S3. Optimized $(TTFH^+)_2(BF4^-)_2$ complex at M06-2X/SVP level. No specific interaction between the $TTFH^+$ units is present. Distances between the cation and anion are indicated, as well as closest cation-cation distance.

Figure S4. Possible intermediate: adduct of $HO_2^\bullet$ on $TTF^{\bullet+}$. M06-2X/SVP geometry, gas phase.

Figure S5. ^{1}H-NMR spectra in d_4-1,2-DCE of (a) dried HTB obtained after biphasic reaction following the Scheme 3 (b) 5mM TTF. The reference in both cases is the first signal corresponding to 6 protons of BA^{+}**.**

Figure S6. ^{1}H-NMR spectra in d_4-1,2-DCE after one-phase reaction between 5 Mm TTF and dried HTB. The dried HTB was obtained using Scheme 3. The reference in all the cases is the first signal corresponding to 6 protons of BA^{+}**.**

Table S1. M06-2X energies for all species.

Table S2. B3LYP-dDsC energies for all species. Contrary to M06-2X/cc-pVTZ, BSSE correction is not equivalent for the two dimers in the tetramer, hence both of them are given.

XYZ coordinates for all stationary points

Full name list of reference 50 and 51.

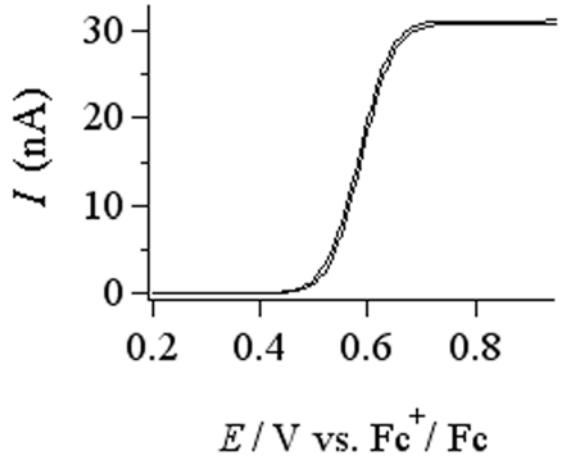

Figure S1. Cyclic voltammogram at Pt microelecrode in the bulk of an organic solution containing 5mm TTF and 5mM BATB in DCE, using Ag/AgCl as the reference electrode and Pt as the counterelectrode.

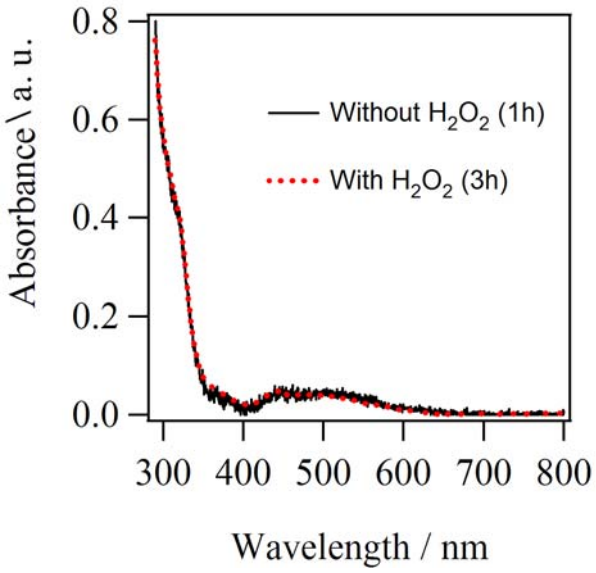

Figure S2. UV-visible spectra of the organic phase after biphasic reaction between 1 mM TTF and 10 mM H_2O_2 under anaerobic conditions (cell II, Scheme 1: TTF=1mM, pH=2).

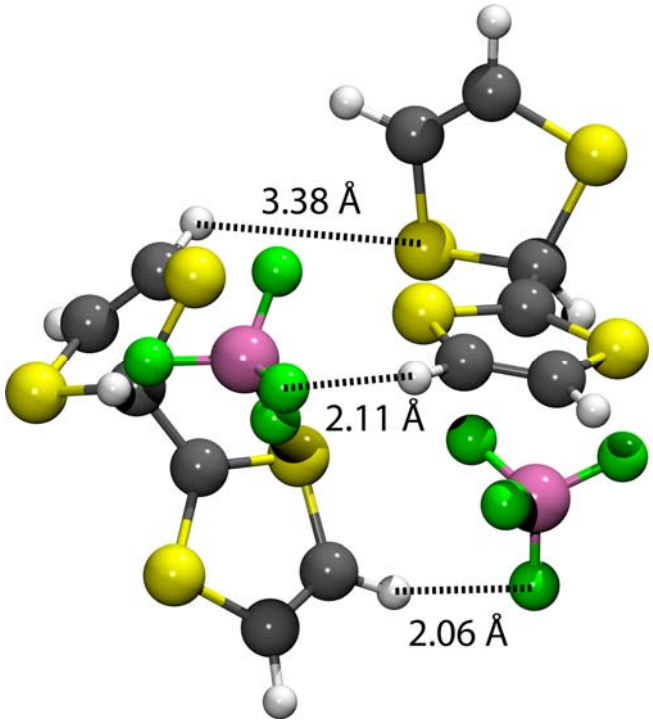

Figure S3. Optimized $(TTFH^{+})_2(BF4^{-})_2$ complex at M06-2X/SVP level. No specific interaction between the $TTFH^{+}$ units is present. Distances between the cation and anion are indicated, as well as closest cation-cation distance.

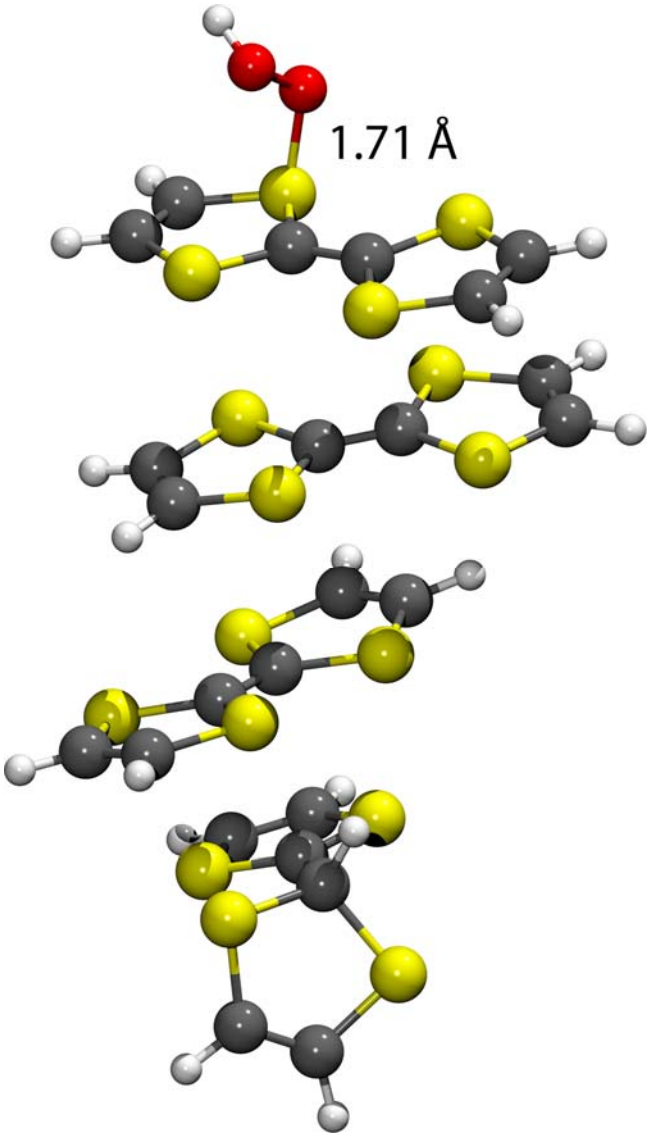

Figure S4. Possible intermediate: adduct of $HO_2^{\bullet}$ on $TTF^{\bullet+}$. M06-2X/SVP geometry, gas phase.

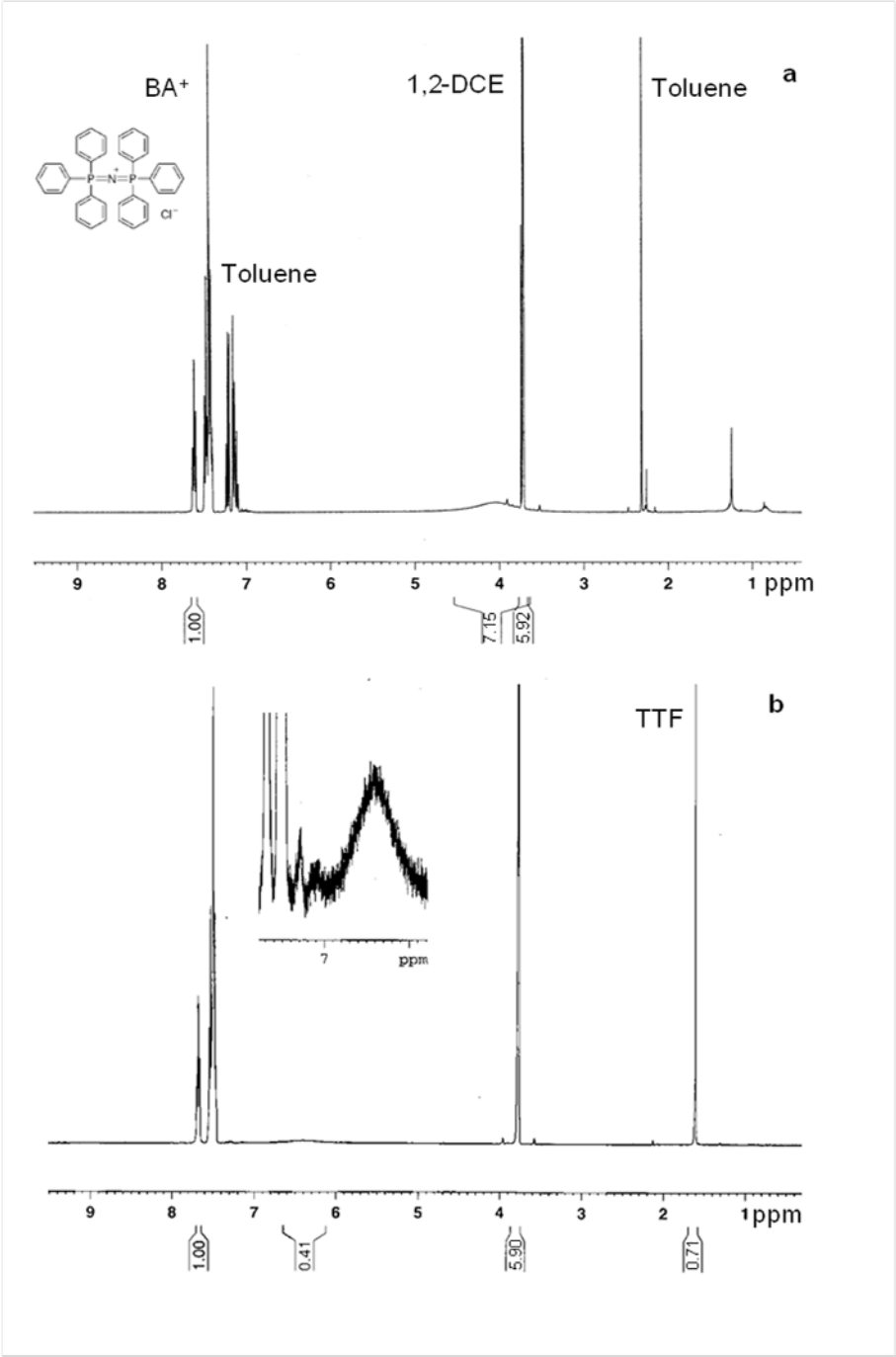

Figure S5. ^{1}H-NMR spectra in d_4-1,2-DCE of (a) dried HTB obtained after biphasic reaction following the Scheme 3 (b) 5mM TTF. The reference in both cases is the first signal corresponding to 6 protons of BA^+**.**

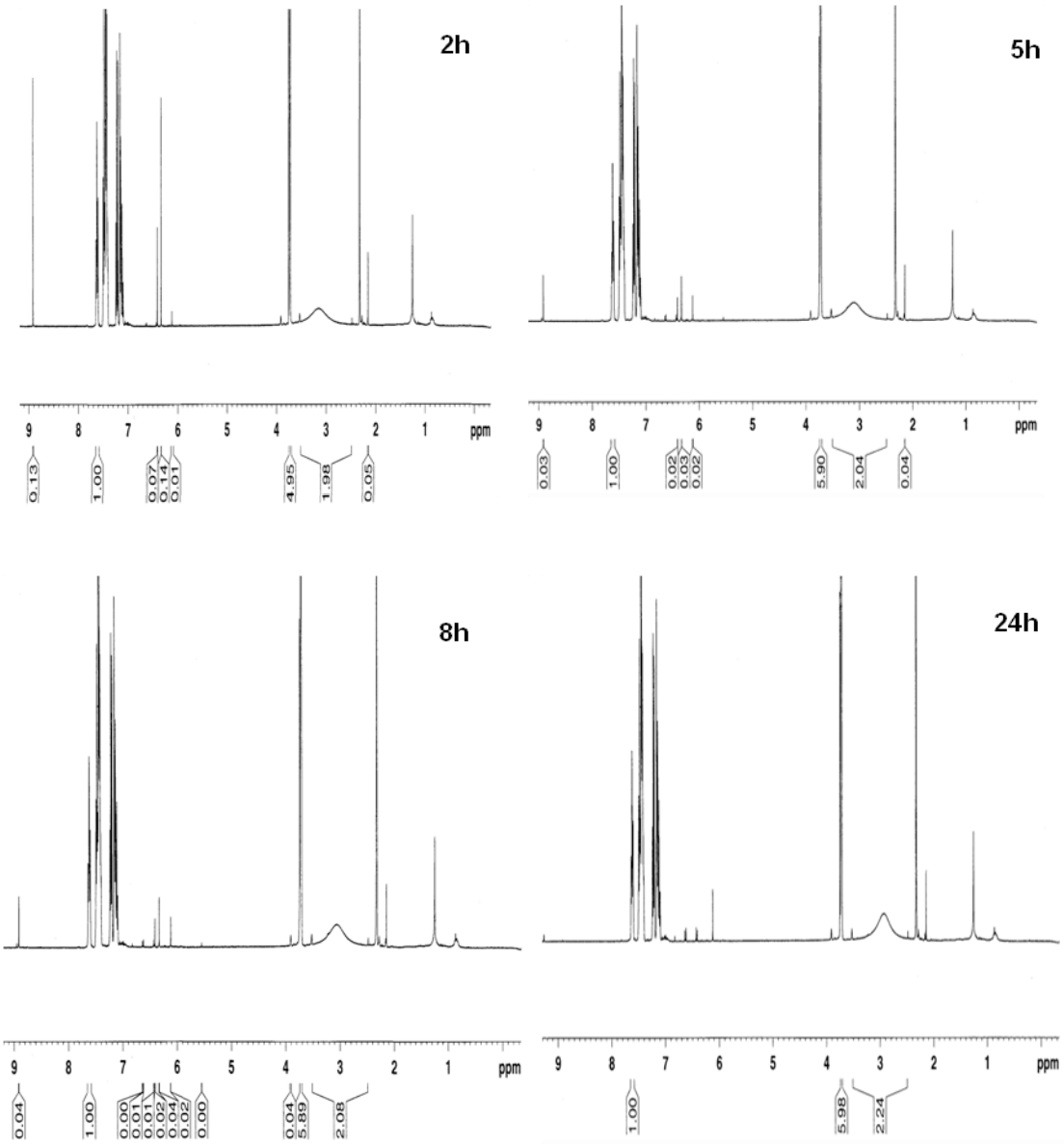

Figure S6. ^{1}H-NMR spectra in d_4-1,2-DCE after one-phase reaction between 5 mM TTF and dried HTB. The dried HTB was obtained using Scheme 3. The reference in all the cases is the first signal corresponding to 6 protons of BA^{+}**.**

Table S1. M06-2X energies for all species

M06-2X	SVP gas phase	Thermal contribution	cc-pVTZ IEFPCM	cc-pVTZ gas phase (monomer basis)	cc-pVTZ gas phase (dimer basis)
O_2	-150.143171	0.007485	-150.321757	-150.321669	-150.323255
TTF	-1822.929300	0.094000	-1823.756441	-1823.749772	-1823.750829
$TTFH^+$	-1823.283876	0.105925	-1824.176343	-1824.105879	-1824.106518
$TTF\text{-}TTFH^+$	-3646.251468	0.201732	-3647.949303	-3647.889431	-3647.890651
$[TTF_4H_2]^{2+}$	-7292.487632	0.405262	-7295.910913	-7295.746876	-7295.747065
$[TTF_4H_2\ldots O_2]^{2+}$ A	-7442.636009	0.413839	-7446.236039	--	--
$[TTF_4H_2\ldots O_2]^{2+}$ B	-7442.636199	0.413992	-7446.235858	--	--
$[TTF_4H_2\ldots O_2]^{2+‡}$	-7442.581210	0.407978	-7446.181217	--	--
$[TTF_4H_2\ldots HO_2]^{2+}$	-7442.631798	0.412658	-7446.230002	--	--
$[(TTFH^+)_2(BF4^-)_2]$ (Fig. S4)	-4495.076824	0.259140	--	--	--
TTFH-OOH (Fig. S5)	-7442.620742	0.414612	--	--	--

Table S2. B3LYP-dDsC energies for all species. Contrary to M06-2X/cc-pVTZ, BSSE correction is not equivalent for the two dimers in the tetramer.

B3LYP-dDsC	6-31+G** gas phase	Thermal contribution	6-31+G** SM8	B3LYP/6-31+G** gas phase (monomer basis)	B3LYP/6-31+G** gas phase (dimer basis)
O_2	-150.327575	0.007087	-150.330200	-150.325483	-150.326664
TTF	-1823.779905	0.093116	-1823.794780	-1823.738708	-1823.740846
$TTFH^+$	-1824.141772	0.105267	-1824.224103	-1824.097950	-1824.099994
$TTF\text{-}TTFH^+$	-3647.955809	0.200284	-3648.033122	-3647.856792	-3647.859810
$TTF\text{-}TTFH^+$	--	--	--	-3647.856793	-3647.859436
$[TTF_4H_2]^{2+}$	-7295.879905	0.402622	-7296.080276	-7295.660178	-7295.660983
$[TTF_4H_2\ldots O_2]^{2+}$ A	-7446.211043	0.409234	-7446.410070	--	--
$[TTF_4H_2\ldots O_2]^{2+}$ B	-7446.211302	--	-7446.411431	--	--
$[TTF_4H_2\ldots O_2]^{2+‡}$	-7446.172892	0.405229	-7446.373664	--	--
$[TTF_4H_2\ldots HO_2]^{2+}$	-7446.213102	0.410069	-7446.409815	--	--

XYZ coordinates of all stationary points

M06-2X geometries

O_2

O	0.000000	0.000000	0.591424
O	0.000000	0.000000	-0.591424

TTF

S	1.632157	1.490530	-0.057416
C	0.673334	0.000001	-0.052091
S	1.632157	-1.490529	-0.057442
C	3.167676	-0.668274	0.140238

C	3.167677	0.668271	0.140250
C	-0.673333	0.000001	-0.052107
S	-1.632155	1.490530	-0.057455
C	-3.167680	0.668271	0.140176
C	-3.167680	-0.668274	0.140163
S	-1.632155	-1.490529	-0.057481
H	-4.060934	1.284771	0.234198
H	-4.060933	-1.284776	0.234174
H	4.060928	1.284771	0.234295
H	4.060928	-1.284776	0.234271

$TTFH^+$

S	1.456941	1.569654	-0.515729
C	0.740040	0.535770	0.829326
S	1.825244	-0.907630	1.108799
C	2.451854	-0.896224	-0.545334
C	2.278490	0.208788	-1.273211
C	-0.642979	0.131428	0.391817
S	-1.964330	1.178218	0.483387
C	-3.086230	0.126197	-0.280546
C	-2.596050	-1.076195	-0.664702
S	-0.939062	-1.371118	-0.311083
H	-3.172528	-1.860486	-1.158150
H	-4.115936	0.463428	-0.410997
H	3.002465	-1.777453	-0.878261
H	2.657207	0.347050	-2.286932
H	0.697359	1.142902	1.744263

$TTF\text{-}TTFH^+$

S	2.786916	-1.329279	-1.615561
C	1.501488	-0.324778	-0.767393
S	2.319494	1.069639	0.070415
C	3.814175	0.158739	0.332556
C	4.024237	-0.917897	-0.428178
C	0.742113	-1.187904	0.201865
S	-0.110948	-2.552575	-0.320663
C	-0.520729	-3.123262	1.248745
C	-0.087404	-2.367835	2.281765
S	0.796689	-0.946782	1.872308
H	-0.264420	-2.582922	3.336096
H	-1.101096	-4.042859	1.333209
H	4.528859	0.551403	1.056788
H	4.929935	-1.525203	-0.404674
H	0.820571	0.068556	-1.540983
S	-0.354722	2.636266	-1.278283
C	-1.108590	1.616339	-0.049054
S	-0.899992	2.175899	1.610592
C	0.037155	3.587826	1.168624
C	0.284289	3.793050	-0.128906
C	-1.834769	0.515088	-0.354690
S	-2.012404	-0.092263	-2.005031
C	-3.183315	-1.329413	-1.579162
C	-3.500079	-1.468680	-0.288183
S	-2.730873	-0.396018	0.868933
H	-3.612863	-1.916073	-2.391298
H	-4.230249	-2.182352	0.094374

H	0.845993	4.637648	-0.527625
H	0.365316	4.245976	1.972804

$[TTF_4H_2]^{2+}$

S	5.475887	1.416831	-1.251616
C	4.965978	-0.330649	-1.186532
S	6.200724	-1.331025	-2.113413
C	7.519641	-0.222205	-1.741551
C	7.197242	1.012852	-1.352146
C	4.886914	-0.838111	0.228501
S	4.373374	-2.410352	0.579185
C	4.717557	-2.345158	2.261517
C	5.220850	-1.174925	2.714150
S	5.429528	0.069375	1.542403
C	1.836256	0.079301	0.309081
S	1.776904	-0.367881	2.020744
C	0.983736	-1.908484	1.731890
C	0.782539	-2.278625	0.462174
S	1.321719	-1.193091	-0.805912
C	2.226816	1.307774	-0.099367
S	2.153248	1.828516	-1.787107
C	2.728138	3.451890	-1.457509
C	3.009850	3.772290	-0.190349
S	2.789314	2.538761	1.036383
H	5.493283	-0.965934	3.749572
H	4.517836	-3.228560	2.869710
H	7.918905	1.806684	-1.155489
H	8.540249	-0.575276	-1.896600
H	3.990434	-0.444642	-1.687051
H	0.289800	-3.202977	0.155641
H	0.674722	-2.491107	2.600293
H	2.835128	4.128668	-2.305544
H	3.373347	4.747437	0.134405
H	-3.990156	0.444501	-1.687885
C	-4.965782	0.330512	-1.187522
C	-4.886989	0.838109	0.227477
S	-5.429804	-0.069281	1.541365
S	-4.373556	2.410395	0.578108
C	-4.718009	2.345330	2.260391
C	-5.221342	1.175120	2.713040
S	-6.200445	1.330710	-2.114705
S	-5.475609	-1.416993	-1.252511
C	-7.519367	0.221920	-1.742771
C	-7.196965	-1.013072	-1.353164
H	-7.918620	-1.806896	-1.156438
H	-8.539972	0.574948	-1.897937
H	-5.493935	0.966209	3.748436
H	-4.518415	3.228789	2.868541
C	-2.226765	-1.307725	-0.099719
C	-1.836321	-0.079205	0.308700
S	-1.777279	0.368106	2.020341
S	-1.321606	1.193111	-0.806297
C	-0.782690	2.278759	0.461803
C	-0.984104	1.908710	1.731511
H	-0.675271	2.491411	2.599926
H	-0.289946	3.203114	0.155289

S	-2.152868	-1.828603	-1.787400
S	-2.789419	-2.538642	1.036032
C	-3.009675	-3.772282	-0.190638
C	-2.727747	-3.451974	-1.457772
H	-2.834551	-4.128825	-2.305772
H	-3.373190	-4.747417	0.134130

$[TTF_4H_2\ldots O_2]^{2+}$ A

S	5.453398	-1.569991	0.976330
C	4.940616	0.170918	1.137448
S	6.137074	1.029430	2.239208
C	7.472514	-0.021077	1.769208
C	7.168233	-1.189526	1.200591
C	4.904230	0.871638	-0.194291
S	4.394210	2.477246	-0.333882
C	4.784750	2.650595	-1.998516
C	5.303887	1.555072	-2.597702
S	5.483732	0.158360	-1.608669
C	1.865144	-0.013862	-0.477309
S	1.833470	0.650778	-2.117091
C	1.044260	2.147064	-1.643113
C	0.821733	2.349342	-0.339708
S	1.330666	1.103599	0.785206
C	2.236083	-1.289969	-0.225764
S	2.110847	-2.030307	1.374897
C	2.704473	-3.595183	0.850899
C	3.016623	-3.747852	-0.440304
S	2.820382	-2.365109	-1.499891
O	-0.093089	-0.584433	3.409369
O	-1.171502	-1.046490	3.565824
H	5.606500	1.494443	-3.643989
H	4.602883	3.611835	-2.481268
H	7.898220	-1.950775	0.922533
H	8.485427	0.303166	2.012455
H	3.948772	0.215248	1.616556
H	0.329121	3.229666	0.076492
H	0.753137	2.838845	-2.434007
H	2.797305	-4.375634	1.606492
H	3.393359	-4.671801	-0.879580
H	-3.873537	-0.659312	1.435563
C	-4.871666	-0.486258	0.999785
C	-4.848450	-0.746076	-0.483173
S	-5.445960	0.364569	-1.602487
S	-4.340568	-2.229645	-1.114487
C	-4.750076	-1.883976	-2.747473
C	-5.275734	-0.659289	-2.975300
S	-6.041934	-1.655925	1.801005
S	-5.408047	1.213845	1.378354
C	-7.397342	-0.534641	1.678937
C	-7.115700	0.755293	1.484508
H	-7.859106	1.552725	1.451206
H	-8.402853	-0.934697	1.818028
H	-5.592455	-0.282064	-3.948683
H	-4.574348	-2.649674	-3.504297
C	-2.195014	1.342742	0.088086
C	-1.812970	0.198920	-0.524861

S	-1.776773	0.047155	-2.288101
S	-1.286643	-1.244395	0.351126
C	-0.769732	-2.101093	-1.088907
C	-0.987072	-1.521746	-2.274698
H	-0.691570	-1.948929	-3.233424
H	-0.275665	-3.064181	-0.950079
S	-2.086321	1.585573	1.835121
S	-2.782803	2.738632	-0.821001
C	-2.989429	3.753955	0.593417
C	-2.682105	3.233779	1.786358
H	-2.779832	3.760174	2.736160
H	-3.367849	4.764714	0.439413

$[TTF_4H_2\ldots O_2]^{2+}$ B

S	-5.483219	-1.720281	-0.847144
C	-4.964417	-0.014334	-1.219900
S	-6.115949	0.685842	-2.469021
C	-7.469861	-0.298137	-1.913342
C	-7.188392	-1.378261	-1.181694
C	-4.979498	0.854406	0.009936
S	-4.505634	2.475506	-0.042414
C	-4.952228	2.849329	1.574376
C	-5.468554	1.827091	2.293536
S	-5.591291	0.312211	1.484350
C	-1.923101	0.063456	0.464328
S	-1.934226	0.992304	1.970369
C	-1.154665	2.400847	1.267876
C	-0.912031	2.389615	-0.047487
S	-1.390546	0.969451	-0.958925
C	-2.284384	-1.238719	0.416602
S	-2.139789	-2.222195	-1.045357
C	-2.734855	-3.687980	-0.288702
C	-3.063834	-3.635715	1.006258
S	-2.884301	-2.101120	1.836516
O	1.722432	-1.885988	-3.377381
O	2.860104	-1.900283	-3.051777
H	-5.804253	1.893167	3.329368
H	-4.804379	3.867951	1.936010
H	-7.929486	-2.096848	-0.829336
H	-8.472649	-0.012177	-2.234102
H	-3.955632	-0.029371	-1.663685
H	-0.417338	3.194747	-0.593543
H	-0.883446	3.217754	1.937145
H	-2.808711	-4.579524	-0.911926
H	-3.439649	-4.480549	1.583720
H	3.846279	-0.859123	-1.200571
C	4.838261	-0.592633	-0.801211
C	4.800914	-0.558604	0.702794
S	5.349916	0.765608	1.591380
S	4.305043	-1.898501	1.605301
C	4.662734	-1.226090	3.145297
C	5.161152	0.030734	3.137163
S	6.020747	-1.885678	-1.354360
S	5.360639	1.004170	-1.503174
C	7.366338	-0.749591	-1.448377
C	7.072796	0.550825	-1.512748

H	7.810027	1.344827	-1.637438
H	8.375900	-1.159180	-1.506731
H	5.444047	0.601389	4.022742
H	4.478061	-1.829916	4.034927
C	2.124506	1.328456	-0.334257
C	1.744793	0.310189	0.470220
S	1.673341	0.468453	2.231863
S	1.259033	-1.273693	-0.148962
C	0.708352	-1.868221	1.406221
C	0.895540	-1.088027	2.476484
H	0.580946	-1.343874	3.488670
H	0.220406	-2.844071	1.427380
S	2.046113	1.236390	-2.098123
S	2.679005	2.878882	0.305800
C	2.895247	3.614263	-1.272102
C	2.615601	2.874945	-2.350319
H	2.720382	3.217390	-3.380050
H	3.254573	4.642936	-1.304607

$[TTF_4H_2\ldots O_2]^{2+\ddagger}$

S	5.540507	1.468616	-1.302974
C	4.999246	-0.270021	-1.367607
S	6.121916	-1.185725	-2.501481
C	7.493234	-0.134139	-2.153086
C	7.234842	1.058702	-1.613439
C	5.031312	-0.919550	-0.010785
S	4.492901	-2.504802	0.224720
C	4.994328	-2.627524	1.863707
C	5.575575	-1.523758	2.385143
S	5.720046	-0.168786	1.333763
C	2.027057	0.047119	0.428398
S	2.104587	-0.555368	2.089928
C	1.224142	-2.034351	1.737545
C	0.903815	-2.281668	0.462362
S	1.387462	-1.107341	-0.748038
C	2.408786	1.301736	0.098844
S	2.203367	1.971164	-1.523725
C	2.831355	3.553159	-1.102814
C	3.223875	3.755897	0.159481
S	3.087851	2.419789	1.286020
O	-4.132367	1.869876	-2.722083
O	-3.508608	0.875469	-2.325993
H	5.948355	-1.432080	3.406179
H	4.821633	-3.565156	2.393812
H	7.987963	1.821320	-1.411121
H	8.486416	-0.480038	-2.443320
H	3.981400	-0.318937	-1.788213
H	0.344015	-3.154790	0.120894
H	0.959155	-2.678509	2.576410
H	2.880729	4.301062	-1.894513
H	3.630955	4.694409	0.536460
H	-4.250536	0.267285	-1.558358
C	-5.339649	0.063916	-0.733029
C	-4.947881	0.790128	0.461680
S	-4.969162	0.116604	2.024484

S	-4.468778	2.423030	0.368012
C	-4.252262	2.638089	2.066907
C	-4.470392	1.552720	2.837377
S	-6.602253	0.865904	-1.735980
S	-5.596761	-1.697609	-0.573513
C	-7.244807	-0.624814	-2.356683
C	-6.806430	-1.775990	-1.822064
H	-7.164184	-2.763558	-2.116652
H	-8.001923	-0.556049	-3.139489
H	-4.353250	1.515920	3.921069
H	-3.945846	3.619773	2.429252
C	-2.101791	-1.218343	0.177498
C	-1.657550	-0.035399	0.666025
S	-1.422541	0.198483	2.408943
S	-1.188156	1.346484	-0.329623
C	-0.512477	2.254978	1.002539
C	-0.627465	1.749327	2.237069
H	-0.242388	2.225369	3.139082
H	-0.020099	3.200073	0.766392
S	-2.126457	-1.656719	-1.537531
S	-2.602163	-2.518226	1.271713
C	-2.711058	-3.735700	0.015521
C	-2.496832	-3.343773	-1.245403
H	-2.557572	-3.999432	-2.114680
H	-2.968684	-4.751839	0.314810

$[TTF_4H\ldots HO_2]^{2+}$

S	-5.504605	0.166941	-1.827578
C	-4.864602	1.200302	-0.469771
S	-5.931417	2.689781	-0.319444
C	-7.362565	1.840641	-0.903793
C	-7.173007	0.705707	-1.580038
C	-4.858294	0.459080	0.840837
S	-4.283043	1.176521	2.259538
C	-4.741231	-0.102836	3.311090
C	-5.338247	-1.163176	2.721907
S	-5.537559	-1.073973	1.014309
C	-1.885495	-0.448283	0.199817
S	-1.885323	-1.434992	1.668388
C	-0.995552	-0.259154	2.622825
C	-0.708367	0.917534	2.055044
S	-1.239519	1.184917	0.405290
C	-2.322552	-0.925411	-0.987614
S	-2.179808	-0.018601	-2.497628
C	-2.879504	-1.284637	-3.489228
C	-3.251953	-2.418540	-2.886231
S	-3.020418	-2.539607	-1.152507
O	3.604731	4.797984	-0.758519
O	4.174549	5.082345	-1.884253
H	-5.692199	-2.054721	3.241462
H	-4.537160	-0.001431	4.377888
H	-7.969547	0.123671	-2.045409
H	-8.335303	2.305627	-0.736861
H	-3.845837	1.539228	-0.720064
H	-0.146494	1.719019	2.538121
H	-0.696478	-0.547008	3.631097

H	-2.980980	-1.088459	-4.556787
H	-3.695689	-3.273462	-3.396745
H	4.058925	6.044268	-2.029627
C	5.039395	-0.052509	-0.600159
C	4.861159	-1.375367	-0.220456
S	5.249032	-1.945732	1.371479
S	4.267704	-2.588653	-1.311549
C	4.483660	-3.909795	-0.208470
C	4.940099	-3.616970	1.020276
S	4.614906	0.531834	-2.176327
S	5.731240	1.134699	0.459210
C	5.228391	2.134197	-1.925450
C	5.736444	2.410892	-0.713570
H	6.129246	3.381693	-0.411128
H	5.141878	2.854421	-2.738989
H	5.120155	-4.345477	1.811012
H	4.245009	-4.912808	-0.563063
C	2.240592	0.529585	0.892172
C	1.774862	-0.589347	0.284655
S	1.634589	-2.134059	1.123563
S	1.265045	-0.620775	-1.401919
C	0.601570	-2.237660	-1.317875
C	0.768268	-2.922455	-0.179899
H	0.403913	-3.935429	-0.008148
H	0.084089	-2.616925	-2.200359
S	2.306115	2.100336	0.093788
S	2.846046	0.517365	2.547231
C	3.042781	2.257265	2.640084
C	2.807977	2.967889	1.530744
H	2.917283	4.048955	1.445511
H	3.374223	2.678484	3.589409

TTFH-OOH (Fig. S5)

S	-5.703717	-0.961289	-1.474606
C	-5.174455	0.660784	-0.836478
S	-6.429435	1.914719	-1.322743
C	-7.746990	0.743021	-1.312730
C	-7.423205	-0.550067	-1.378404
C	-5.037372	0.655298	0.662129
S	-4.496816	2.015668	1.507817
C	-4.777343	1.378377	3.079033
C	-5.273631	0.121616	3.124207
S	-5.534645	-0.649820	1.607062
C	-1.994798	-0.200615	0.288911
S	-1.842909	-0.329851	2.047404
C	-1.063861	1.234247	2.233293
C	-0.925863	1.996209	1.142633
S	-1.532544	1.370268	-0.379457
C	-2.411660	-1.233756	-0.477584
S	-2.419933	-1.174908	-2.243602
C	-3.006002	-2.815263	-2.436793
C	-3.230173	-3.535125	-1.332510
S	-2.930481	-2.773033	0.217927
C	2.008667	1.326571	0.083488
S	1.872124	2.321668	-1.372609

C	2.452064	3.785464	-0.597096
C	2.809512	3.718304	0.689991
S	2.676784	2.163191	1.494248
C	1.639987	0.030993	0.140355
S	1.724380	-0.887103	1.648484
C	0.950840	-2.315039	0.986585
C	0.655819	-2.311181	-0.319245
S	1.088490	-0.899333	-1.256728
C	4.801738	-0.798532	-0.003926
S	5.362636	-0.542231	1.599534
C	4.993824	-2.142210	2.157412
C	4.594657	-3.014801	1.203643
S	4.358940	-2.457810	-0.393343
C	4.866378	0.207106	-0.958166
S	5.515289	1.780535	-0.654165
C	5.322356	2.366583	-2.278408
C	4.805816	1.513577	-3.173462
S	4.357530	-0.059070	-2.586891
H	-5.510102	-0.429332	4.035419
H	-4.548047	2.002136	3.944142
H	-8.145149	-1.365229	-1.440772
H	-8.768686	1.125569	-1.306786
H	-4.216511	0.940955	-1.305029
H	-0.440555	2.973401	1.125052
H	-0.705155	1.507423	3.225949
H	-3.162460	-3.176490	-3.453437
H	-3.590083	-4.564048	-1.328238
H	5.651929	3.384028	-2.490695
H	4.643972	1.727060	-4.230216
H	5.123927	-2.355968	3.217147
H	4.376895	-4.065224	1.409201
H	0.723964	-3.134129	1.669089
H	0.164048	-3.132328	-0.843108
H	2.484054	4.694242	-1.199069
H	3.176179	4.561068	1.276327
O	7.066489	-0.517982	1.474817
O	7.504890	-1.591269	0.683376
H	8.101856	-2.054100	1.294882

$[(TTFH^{+})_2(BF4^{-})_2]$ (Fig. S4)

S	-3.562874	0.806317	1.402745
S	-1.024627	-0.476530	1.162712
S	-1.578233	-1.501311	-1.727914
S	-4.227537	-2.073475	-0.527852
C	-2.472356	1.048757	2.699153
C	-1.266039	0.443132	2.588546
C	-2.538738	-0.179144	0.503651
C	-2.974654	-0.763385	-0.814330
C	-3.020553	-3.358904	-0.470274
C	-1.830498	-3.100563	-1.019167
H	-2.779263	1.683386	3.529691
H	-0.443374	0.501767	3.307002
H	-3.410763	0.036271	-1.428879
H	-3.303365	-4.311918	-0.022972
H	-1.017623	-3.825924	-1.076701

S	1.080086	0.900628	-1.226946
S	3.396931	2.113523	-0.075454
S	4.455813	-1.032598	-1.408905
S	1.883209	-1.964049	-0.259427
C	1.121466	2.619911	-1.255618
C	2.217318	3.193284	-0.708670
C	2.574319	0.704013	-0.486181
C	3.149324	-0.650911	-0.178570
C	2.177096	-2.267055	-1.975722
C	3.332514	-1.846152	-2.498286
H	0.261804	3.150174	-1.676445
H	2.388656	4.265798	-0.624049
H	3.569752	-0.658743	0.839128
H	1.423053	-2.820012	-2.538052
H	3.640520	-2.004677	-3.531761
F	0.980055	-1.567288	2.695232
F	3.148069	-0.812242	2.822368
F	1.528085	0.451833	1.832835
F	1.487577	0.165624	4.094316
B	1.807125	-0.459328	2.900662
F	-1.739972	3.600326	-1.902322
F	-3.421849	2.208756	-1.147729
F	-1.492726	2.472445	0.067655
F	-1.454595	1.333322	-1.898053
B	-2.051258	2.437512	-1.217901

B3LYP-dDsC geometries

O_2

O	0.000000	0.000000	0.607267
O	0.000000	0.000000	-0.607267

TTF

S	1.642703	-1.492200	0.143104
C	0.673267	0.000000	0.141268
S	1.642703	1.492200	0.143104
C	3.166049	0.667787	-0.174173
C	3.166049	-0.667787	-0.174173
C	-0.673267	0.000000	0.141268
S	-1.642703	-1.492200	0.143104
C	-3.166049	-0.667787	-0.174173
C	-3.166049	0.667787	-0.174173
S	-1.642703	1.492200	0.143104
H	-4.040898	-1.285733	-0.330508
H	-4.040898	1.285733	-0.330508
H	4.040898	-1.285733	-0.330508
H	4.040898	1.285733	-0.330508

$TTFH^+$

S	1.424097	1.543005	-0.574259
C	0.730996	0.534763	0.818395
S	1.832187	-0.907028	1.114946
C	2.500826	-0.893592	-0.526559
C	2.308978	0.190457	-1.281286

C	-0.651242	0.132621	0.395713
S	-1.995813	1.163188	0.553444
C	-3.118276	0.121333	-0.251571
C	-2.620241	-1.056265	-0.689419
S	-0.945660	-1.356568	-0.363081
H	-3.187247	-1.822746	-1.203898
H	-4.144339	0.453335	-0.355202
H	3.072094	-1.762976	-0.829253
H	2.685403	0.317246	-2.289021
H	0.700722	1.157556	1.713695

TTF-TTFH^{+}

S	2.351757	-1.885270	-1.705890
C	1.438472	-0.547569	-0.811442
S	2.606237	0.837114	-0.521598
C	4.022777	-0.229990	-0.456062
C	3.907580	-1.447781	-0.988550
C	0.855540	-1.054158	0.473362
S	-0.146368	-2.437275	0.525397
C	-0.265142	-2.508409	2.251503
C	0.393289	-1.549487	2.930980
S	1.254577	-0.375200	1.988004
H	0.419788	-1.454879	4.009313
H	-0.852897	-3.304683	2.690744
H	4.932993	0.174834	-0.031398
H	4.709165	-2.173599	-1.048999
H	0.644923	-0.207028	-1.485241
S	-0.341814	2.679056	-0.806634
C	-1.301737	1.485262	0.080627
S	-1.414579	1.784213	1.814809
C	-0.498537	3.283078	1.774943
C	-0.005427	3.676291	0.597101
C	-1.941104	0.464577	-0.553358
S	-1.792853	0.216070	-2.301199
C	-2.960299	-1.093884	-2.368793
C	-3.518736	-1.487656	-1.220132
S	-3.016236	-0.677323	0.253771
H	-3.181931	-1.510279	-3.343168
H	-4.258654	-2.272348	-1.126632
H	0.578792	4.573551	0.437418
H	-0.374805	3.813105	2.710519

$[TTF_4H_2]^{2+}$

S	5.474532	-0.587430	2.284880
C	5.000851	0.777010	1.153750
S	5.898847	2.304387	1.686121
C	7.258157	1.400394	2.365932
C	7.070730	0.107512	2.633872
C	5.320563	0.446052	-0.274129
S	5.047546	1.554520	-1.540211
C	5.754934	0.584379	-2.786353
C	6.240548	-0.612580	-2.399294
S	6.074138	-1.014612	-0.720973
C	1.931556	-0.042141	-0.560151
S	1.876231	0.430169	-2.261468
C	1.048967	1.951251	-1.965880

C	0.838437	2.307950	-0.694871
S	1.391435	1.216533	0.563228
C	2.329449	-1.266571	-0.130791
S	2.249031	-1.738237	1.575494
C	2.720257	-3.406261	1.289553
C	3.006566	-3.769876	0.035878
S	2.915382	-2.533952	-1.213276
H	6.720279	-1.332299	-3.051115
H	5.777630	0.981327	-3.793706
H	7.805112	-0.541613	3.094534
H	8.170240	1.948152	2.569249
H	3.931585	0.982589	1.264884
H	0.350198	3.220743	-0.379431
H	0.759278	2.535324	-2.829686
H	2.763097	-4.062277	2.149927
H	3.315220	-4.761862	-0.268683
H	-3.931607	-0.982977	1.264420
C	-5.000885	-0.777424	1.153373
C	-5.320660	-0.446128	-0.274424
S	-6.074032	1.014740	-0.720940
S	-5.047614	-1.554264	-1.540787
C	-5.755002	-0.583812	-2.786689
C	-6.240426	0.613139	-2.399369
S	-5.898865	-2.304909	1.685464
S	-5.474570	0.586733	2.284833
C	-7.258331	-1.400986	2.365051
C	-7.070919	-0.108149	2.633224
H	-7.805387	0.540961	3.093770
H	-8.170495	-1.948740	2.568014
H	-6.720063	1.333071	-3.051024
H	-5.777754	-0.980532	-3.794130
C	-2.329566	1.266580	-0.130546
C	-1.931618	0.042273	-0.560209
S	-1.876226	-0.429598	-2.261650
S	-1.391496	-1.216680	0.562862
C	-0.838433	-2.307759	-0.695505
C	-1.048927	-1.950732	-1.966428
H	-0.759194	-2.534571	-2.830376
H	-0.350183	-3.220620	-0.380282
S	-2.249270	1.737785	1.575871
S	-2.915472	2.534239	-1.212725
C	-3.006795	3.769813	0.036765
C	-2.720553	3.405870	1.290358
H	-2.763480	4.061651	2.150907
H	-3.315473	4.761870	-0.267542

$[TTF_4H_2...O_2]^{2+}$ A

S	-5.402152	-2.296471	0.297816
C	-4.945817	-0.977952	-0.892827
S	-5.812368	-1.320271	-2.490545
C	-7.163216	-2.149757	-1.706151
C	-6.981948	-2.586291	-0.459112
C	-5.306493	0.382792	-0.374894
S	-5.065318	1.793643	-1.301258
C	-5.813602	2.877930	-0.179118
C	-6.293936	2.320281	0.950600

S	-6.081690	0.608248	1.124932
C	-1.940719	0.697523	0.166406
S	-1.919875	2.452069	-0.038109
C	-1.117903	2.411171	-1.600086
C	-0.884798	1.214491	-2.148385
S	-1.382375	-0.208288	-1.249925
C	-2.327624	0.078595	1.310758
S	-2.206650	-1.677204	1.521366
C	-2.747133	-1.663344	3.192674
C	-3.063030	-0.485822	3.739388
S	-2.941599	0.945135	2.723152
O	-0.006735	-3.492577	-0.536371
O	1.062778	-3.654096	0.017233
H	-6.795675	2.855687	1.747203
H	-5.862802	3.928517	-0.437313
H	-7.710667	-3.148553	0.111585
H	-8.064052	-2.298743	-2.288860
H	-3.871976	-1.032456	-1.097375
H	-0.406067	1.053246	-3.105447
H	-0.859692	3.360642	-2.050846
H	-2.798020	-2.616627	3.703628
H	-3.407163	-0.344745	4.756106
H	3.823398	-1.285789	0.684219
C	4.899189	-1.170919	0.519762
C	5.260925	0.283816	0.457301
S	6.041233	0.968564	-0.892920
S	5.014815	1.331617	1.779508
C	5.761514	2.714912	1.055692
C	6.247051	2.540534	-0.189949
S	5.747024	-1.996306	1.940792
S	5.371357	-2.051904	-1.017915
C	7.108029	-2.542902	0.952315
C	6.942293	-2.567381	-0.370725
H	7.678464	-2.925486	-1.079702
H	8.001776	-2.869275	1.469927
H	6.749526	3.299627	-0.776706
H	5.806560	3.631795	1.630234
C	2.296274	0.551710	-1.234117
C	1.908433	0.797117	0.043110
S	1.886890	2.411497	0.761009
S	1.357749	-0.488816	1.129514
C	0.845112	0.603112	2.403539
C	1.074471	1.909112	2.234973
H	0.808223	2.682340	2.943953
H	0.360874	0.164022	3.265899
S	2.187607	-1.058261	-1.967152
S	2.900639	1.809712	-2.318701
C	3.004366	0.760571	-3.726732
C	2.698239	-0.529674	-3.562496
H	2.742482	-1.280647	-4.341275
H	3.332440	1.208131	-4.656318

$[TTF_4H_2\ldots O_2]^{2+}$ B

S	5.490229	-1.541893	1.686351
C	5.015600	0.200994	1.366361
S	5.967115	1.277435	2.534588

C	7.320754	0.147191	2.652739
C	7.110371	-1.113465	2.271369
C	5.300517	0.599580	-0.050852
S	4.957866	2.162591	-0.640404
C	5.697274	1.938126	-2.187727
C	6.247247	0.727293	-2.410937
S	6.123484	-0.432099	-1.126343
C	2.020462	0.162863	-0.690873
S	2.034175	1.069103	-2.208616
C	1.184101	2.463011	-1.557019
C	0.915457	2.471317	-0.248272
S	1.435740	1.087307	0.700139
C	2.392995	-1.137973	-0.588876
S	2.200178	-2.061277	0.912044
C	2.766533	-3.575684	0.225557
C	3.137754	-3.581621	-1.058367
S	3.054776	-2.063076	-1.941725
O	-1.392099	-1.744318	3.256783
O	-2.538209	-2.034267	2.972875
H	6.752132	0.428473	-3.321304
H	5.683149	2.764899	-2.887053
H	7.841198	-1.910025	2.337174
H	8.250759	0.522741	3.061834
H	3.954745	0.333989	1.596382
H	0.405871	3.268119	0.277429
H	0.919325	3.251599	-2.249386
H	2.790155	-4.437492	0.880556
H	3.504666	-4.448041	-1.593903
H	-3.870884	-1.032451	1.031314
C	-4.919649	-0.775513	0.861999
C	-5.138650	-0.342830	-0.556470
S	-5.933125	1.112847	-0.938862
S	-4.749249	-1.344916	-1.880413
C	-5.431764	-0.315693	-3.091409
C	-5.990600	0.829216	-2.649371
S	-5.912013	-2.297521	1.221131
S	-5.423823	0.524522	2.052818
C	-7.278988	-1.390313	1.877835
C	-7.063309	-0.127233	2.248011
H	-7.802901	0.518397	2.705326
H	-8.222347	-1.912623	1.980869
H	-6.463414	1.576164	-3.275032
H	-5.377579	-0.634883	-4.124821
C	-2.234585	1.374301	-0.004590
C	-1.843103	0.337298	-0.787312
S	-1.778174	0.422376	-2.552396
S	-1.320847	-1.214548	-0.118790
C	-0.729226	-1.844399	-1.647169
C	-0.933607	-1.107670	-2.743015
H	-0.624610	-1.383924	-3.742806
H	-0.235286	-2.807062	-1.628644
S	-2.131105	1.326466	1.763932
S	-2.835401	2.900654	-0.664050
C	-2.943921	3.705303	0.895901
C	-2.639221	2.993116	1.985129
H	-2.689641	3.364029	3.001117

H	-3.276342	4.735625	0.901411

$[TTF_4H_2\ldots O_2]^{2+\ddagger}$

S	5.467963	-0.896889	2.171147
C	5.035637	0.680490	1.339285
S	5.912240	2.053163	2.219446
C	7.243078	1.015999	2.746688
C	7.046885	-0.302926	2.724970
C	5.416249	0.661487	-0.111126
S	5.150052	2.000077	-1.132777
C	5.956989	1.338644	-2.513062
C	6.477517	0.104410	-2.357748
S	6.252564	-0.646927	-0.811094
C	2.076036	0.136559	-0.645795
S	2.077778	0.912096	-2.232325
C	1.191973	2.333491	-1.703586
C	0.913514	2.443866	-0.400932
S	1.445913	1.151817	0.660883
C	2.489459	-1.138060	-0.428316
S	2.321080	-1.925503	1.150319
C	2.895975	-3.489771	0.597187
C	3.268470	-3.604300	-0.681156
S	3.178636	-2.165292	-1.689455
O	-3.848413	-2.207386	2.476437
O	-3.421738	-1.023127	2.238361
H	7.016548	-0.446091	-3.118916
H	6.005680	1.937700	-3.413940
H	7.763078	-1.040953	3.064500
H	8.146390	1.501028	3.096066
H	3.963001	0.868580	1.448620
H	0.378243	3.268307	0.051870
H	0.918660	3.057809	-2.459715
H	2.924581	-4.291235	1.324701
H	3.642881	-4.510043	-1.140984
H	-4.336163	-0.478966	1.595332
C	-5.489238	-0.279034	0.927174
C	-5.237047	-0.836428	-0.376063
S	-5.384135	0.053552	-1.840849
S	-4.766643	-2.482755	-0.559172
C	-4.743942	-2.458849	-2.297619
C	-5.006603	-1.279709	-2.888242
S	-6.596980	-1.245975	2.004776
S	-5.843267	1.483626	0.998012
C	-7.266806	0.148879	2.802024
C	-6.946213	1.370803	2.346583
H	-7.317452	2.299037	2.763105
H	-7.926039	-0.034699	3.642470
H	-4.999508	-1.095853	-3.955059
H	-4.504468	-3.379938	-2.813610
C	-2.197556	1.314396	-0.185868
C	-1.782623	0.166526	-0.788890
S	-1.665224	0.063621	-2.554553
S	-1.263453	-1.291859	0.057195
C	-0.615313	-2.064869	-1.373455
C	-0.814122	-1.468577	-2.555485

H	-0.487686	-1.857840	-3.511102
H	-0.106924	-3.010500	-1.236079
S	-2.178468	1.616004	1.555386
S	-2.747427	2.692027	-1.151751
C	-2.749865	3.824616	0.188353
C	-2.488860	3.335802	1.406838
H	-2.494423	3.916878	2.320716
H	-2.993978	4.856658	-0.029558

$[TTF_4H\ldots HO_2]^{2+}$

S	-5.487093	-1.205799	1.920869
C	-4.938709	-1.348420	0.175992
S	-5.770329	-2.823840	-0.568473
C	-7.179547	-2.700536	0.492709
C	-7.055244	-1.976766	1.605984
C	-5.260288	-0.109165	-0.606134
S	-4.928478	0.017203	-2.273608
C	-5.676775	1.562184	-2.491137
C	-6.221541	2.115465	-1.388697
S	-6.082718	1.212834	0.085227
C	-1.910422	0.532746	-0.343345
S	-1.835595	1.443841	-1.854069
C	-0.944110	0.208614	-2.728114
C	-0.718719	-0.952950	-2.106253
S	-1.317131	-1.131513	-0.466010
C	-2.359642	1.052460	0.827293
S	-2.296369	0.143697	2.347110
C	-2.850247	1.481454	3.341819
C	-3.152385	2.631661	2.732100
S	-2.997143	2.692724	0.980938
O	2.599149	-4.999421	0.701471
O	3.790641	-5.294503	1.213649
H	-6.732164	3.070038	-1.356134
H	-5.674832	1.997063	-3.482975
H	-7.825354	-1.862527	2.358800
H	-8.068821	-3.249630	0.208232
H	-3.862422	-1.545178	0.150880
H	-0.187833	-1.793411	-2.534048
H	-0.626078	0.444246	-3.735335
H	-2.927200	1.306531	4.407578
H	-3.509236	3.524108	3.230381
H	3.681006	-6.180086	1.623750
C	5.278555	-0.083604	0.621382
C	5.161659	1.251923	0.314434
S	5.601240	1.901133	-1.251853
S	4.628670	2.449587	1.477695
C	4.946686	3.822480	0.445211
C	5.394074	3.574152	-0.793454
S	4.829879	-0.737985	2.182283
S	5.946014	-1.256214	-0.496407
C	5.404353	-2.353204	1.849512
C	5.905278	-2.589503	0.629883
H	6.273748	-3.546785	0.285333
H	5.301895	-3.091716	2.633197
H	5.630462	4.326991	-1.534617
H	4.771592	4.807775	0.858078

C	2.367620	-0.506954	-0.937110
C	1.939974	0.612379	-0.288068
S	1.845568	2.190419	-1.067243
S	1.392510	0.591331	1.384703
C	0.766751	2.226130	1.355590
C	0.976415	2.951296	0.250145
H	0.656745	3.975772	0.110693
H	0.255288	2.578388	2.241741
S	2.350928	-2.107365	-0.197783
S	2.954421	-0.467682	-2.596469
C	3.043160	-2.211802	-2.760452
C	2.779621	-2.948528	-1.674120
H	2.828063	-4.027135	-1.617805
H	3.342308	-2.607108	-3.722950

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