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

Supporting Information

Interaction of Light with Non-Covalent Zinc Porphyrin-Graphene Oxide Nanohybrid

Ewelina Gacka[1], Gotard Burdzinski[2], Bronisław Marciniak[1,3], Adam Kubas[4,,] Anna Lewandowska-Andralojc[1,3*]*

[1]Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznanskiego 8, 61-614 Poznan, Poland

[2]Faculty of Physics, Adam Mickiewicz University, Uniwersytetu Poznanskiego 2, 61-614 Poznan

[3]Center for Advanced Technology, Adam Mickiewicz University, Uniwersytetu Poznanskiego 10, 61-614 Poznan, Poland

[4]Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

alewand@amu.edu.pl, akubas@ichf.edu.pl

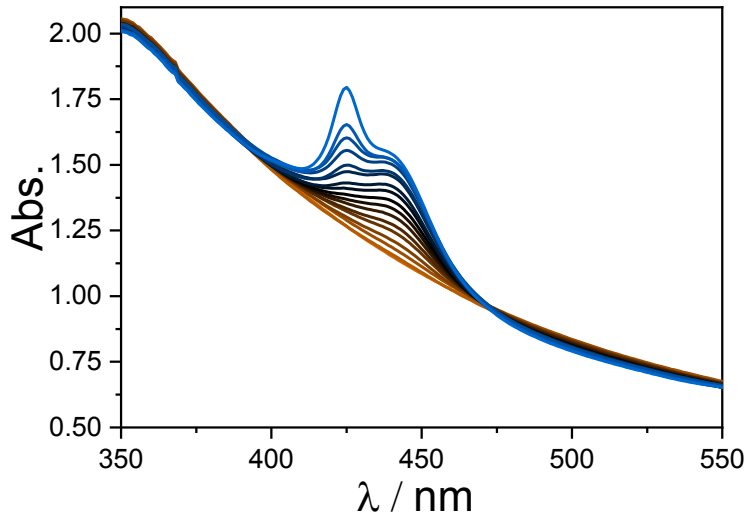

Figure S1. Absorption spectra recorded during addition of EtOH-H_2O (1:2 v/v) solution of TPPH (0-2.7 μM) to 0.1 mg mL^{-1} GO in H_2O (3 mL).

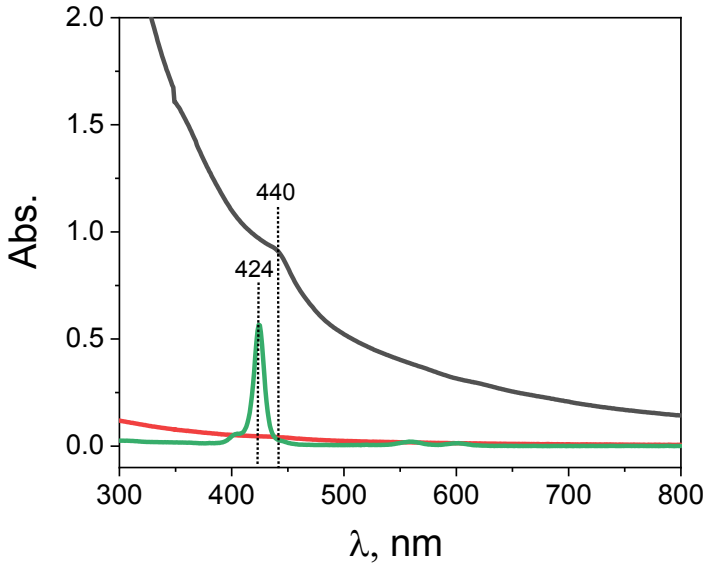

Figure S2. Absorption spectrum of ZnTPPH with the addition of GO suspension (black line), spectrum of the supernatant after centrifuging (red line), spectrum of ZnTPPH before addition of GO (green line).

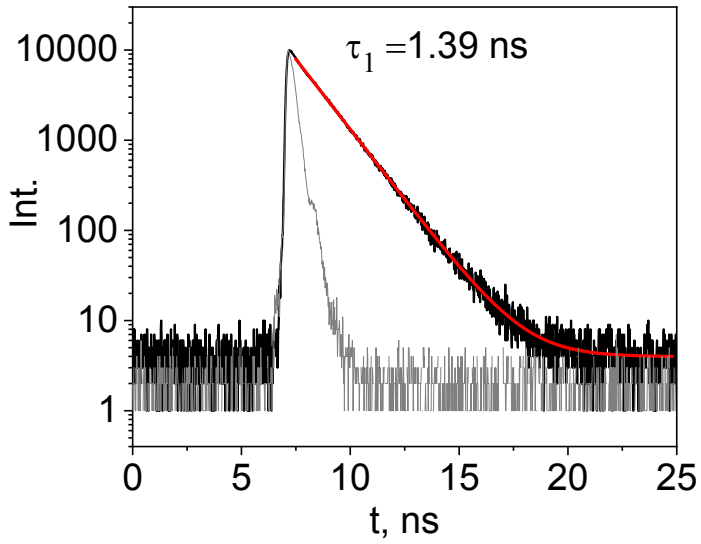

Figure S3 Decay of ZnTPPH fluorescence (black), prompt (grey), λ_{ex} = 405 nm, λ_{em} = 612 nm, monoexponential fit to the decay profile (red).

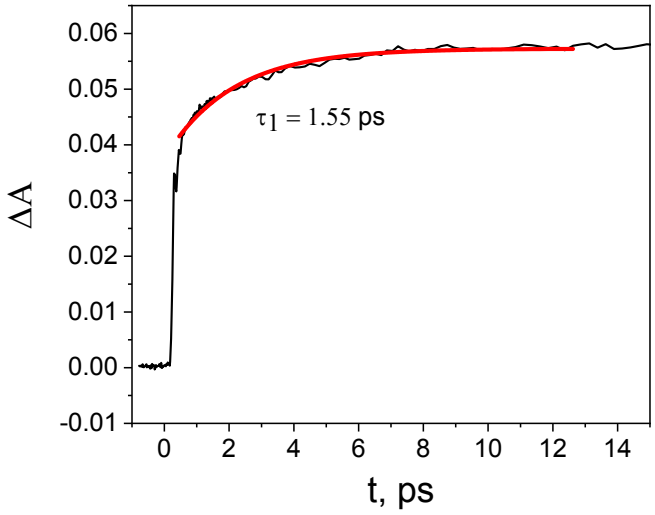

Figure S4 Transient absorption decay at 455 nm at early time delays in EtOH-H_2O (1:2 v/v) recorded for ZnTPPH following 425 nm laser excitation, red-monoexponential fit to the decay profile.

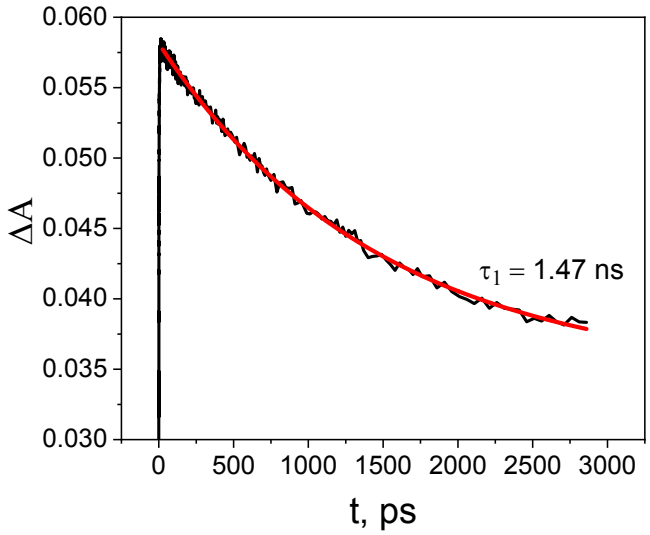

Figure S5 Transient absorption decays at 455 nm in EtOH-H_2O (1:2 v/v) recorded for ZnTPPH following 425 nm laser excitation, red-monoexponential fit to the decay profile.

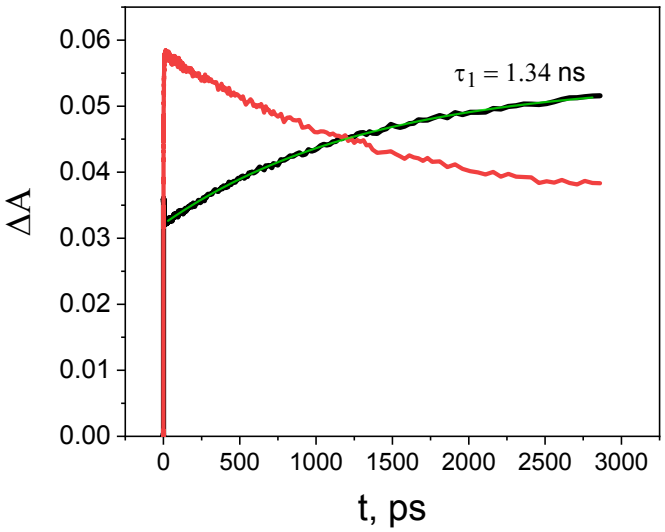

Figure S6 Comparison of transient absorption kinetics: decay at 455 nm (red) and rise at 482 nm (black) in EtOH-H_2O (1:2 v/v) recorded for ZnTPPH following 425 nm laser excitation, green-monoexponential fit to the growth profile at 482 nm.

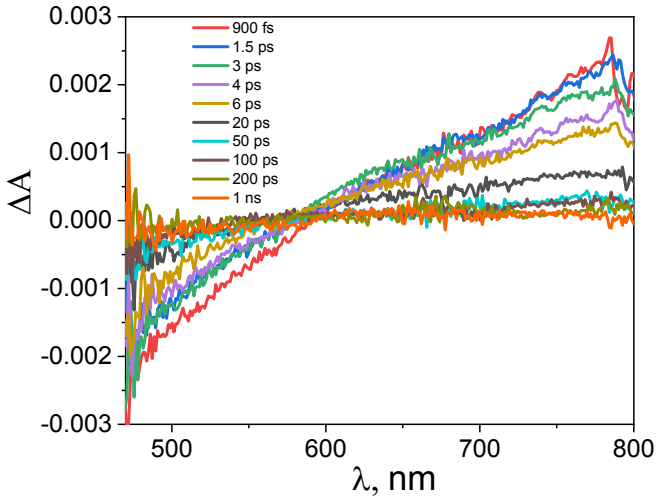

Figure S7 Transient absorption spectra registered at various time delays for GO (1.0 mg mL^{-1}) in water following 442 nm laser excitation.

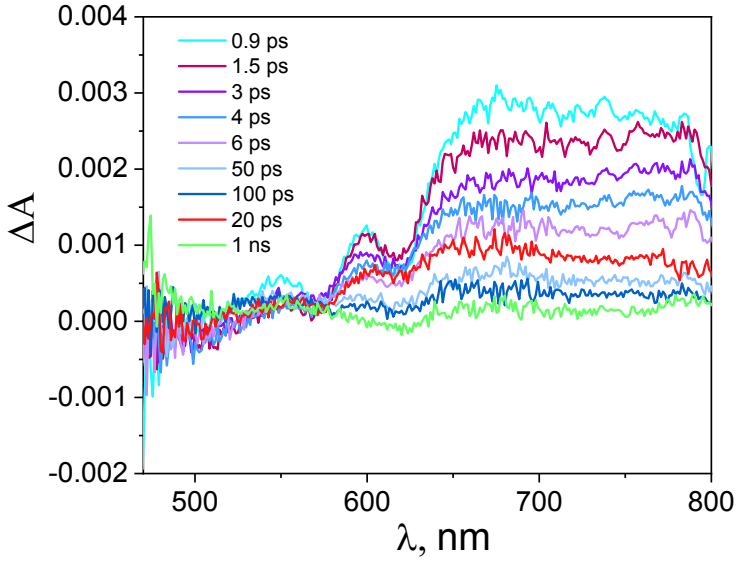

Figure S8 Transient absorption spectra registered at various time delays for ZnTPPH-GO (ZnTPPH concentration 10.0 μM, GO – 0.4 mg mL^{-1}) in EtOH-H_2O (1:2 v/v) following 442 nm laser excitation without correction for the transient absorbance of the GO itself.

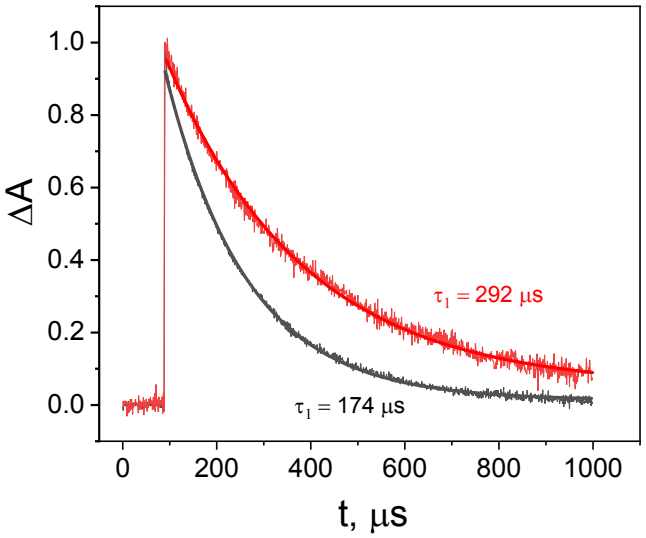

Figure S9. Normalized decay profiles monitored at 480 nm obtained during nanosecond laser flash photolysis (with excitation at 532 nm) of deoxygenated solutions of ZnTPPH (35 μM) (black) and for ZnTPPH in the presence of GO (0.02 mg mL^{-1}) (red).

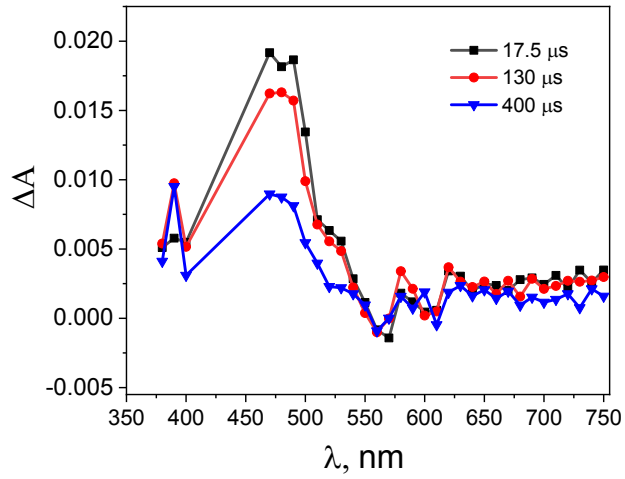

Figure S10 Transient absorption spectra obtained during laser flash photolysis (with excitation at 532 nm) of deoxygenated solutions of ZnTPPH (35 μM) in EtOH-H_2O (1:2 v/v) in the presence of GO (0.02 mg mL^{-1}) after different time delays.

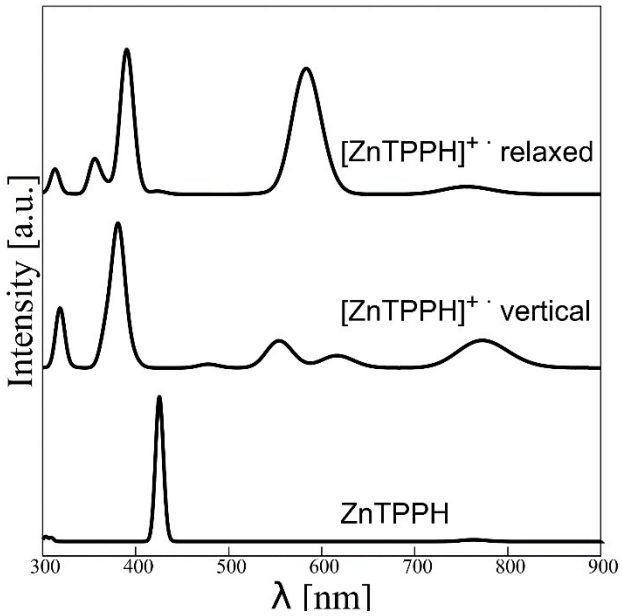

Figure S11. Comparison of computed absorption spectra for neutral ZnTPPH (bottom) with ZnTPPH radical cation spectra at the geometry of the neutral species (vertical detachment, middle) and at the optimized geometry (adiabatic detachment, top).

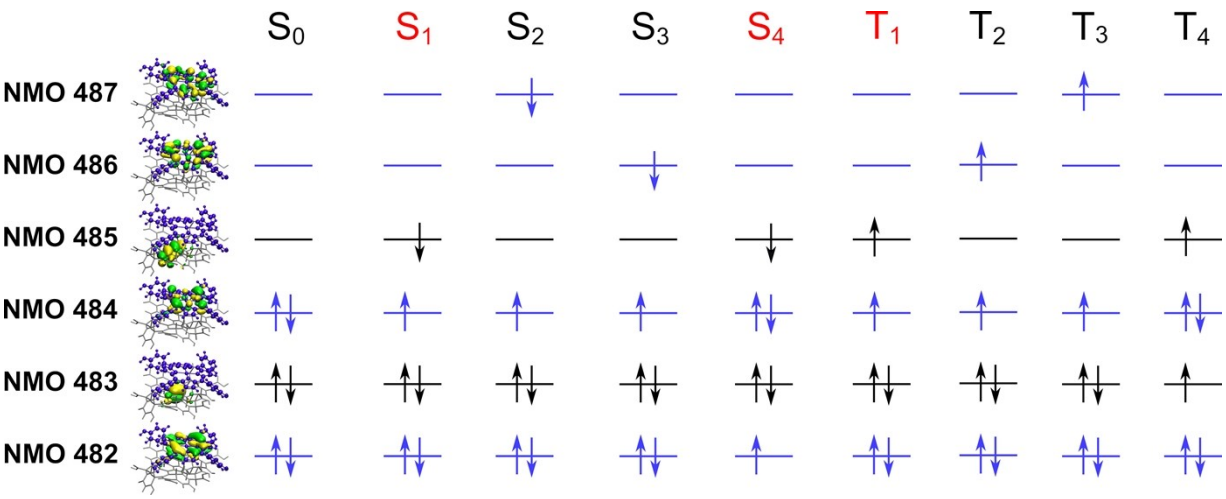

Figure S12. Dominant configurations for selected states in the CASSCF(6,6) wave function. Occupations are provided for natural molecular orbitals (NMOs) 482 – 487 (left) that form the

active space. ZnTPPH-centered and GO-centered NMOs are given in blue and black, respectively. CT states are marked in red.

Cartesian coordinates

ZnTPPH-GO

C	12.823895	-18.558708	1.076075
C	11.921374	-17.552965	0.484931
C	12.689633	-19.861179	0.719530
C	10.845991	-18.019333	-0.503114
C	11.658834	-20.346257	-0.162149
C	10.801794	-19.503300	-0.782470
C	13.936741	-16.645736	2.340127
C	13.760182	-15.839373	1.046846
C	13.916890	-18.166587	2.046185
C	12.405379	-16.157051	0.421914
C	14.871874	-14.555946	3.667589
C	14.695120	-13.758919	2.385082
C	14.597685	-16.050313	3.546942
C	14.028384	-14.341210	1.181096
C	16.176872	-12.667960	4.616342
C	15.326062	-11.746363	3.817571
C	16.097734	-14.032646	4.382358
C	14.611517	-12.273456	2.640703
C	17.112439	-10.762057	5.818883
C	16.454577	-9.859314	4.904350
C	17.029045	-12.119817	5.615549
C	15.668329	-10.315960	3.901811
C	15.163598	-9.400720	2.845153
C	14.577980	-9.949941	1.567196
C	14.482566	-11.459694	1.381101
C	13.292201	-11.957165	0.595111
C	13.234495	-13.426823	0.318971
C	12.295348	-13.882093	-0.572339
C	11.924373	-15.272154	-0.674060
C	11.115175	-15.780337	-1.676258
C	10.747140	-17.169798	-1.753891
C	10.140342	-17.711885	-2.866649
C	9.784475	-19.884357	-1.752513
C	9.516062	-18.996409	-2.764957
C	10.571799	-14.891238	-2.728588
C	10.137461	-15.458672	-4.041729
C	9.973058	-16.968392	-4.173784
C	11.601821	-12.911341	-1.461396
C	10.848365	-13.440605	-2.603561
C	12.605892	-11.009338	-0.294692
C	12.195873	-11.525632	-1.639701
C	13.745208	-9.081548	0.720680
C	12.888184	-9.564118	-0.203413
C	10.409516	-14.682794	-5.267971
C	10.808791	-15.343242	-6.383514
C	10.703010	-17.548961	-5.363748
C	11.000820	-16.773769	-6.433449
C	10.865580	-12.569513	-3.825083
C	10.640774	-13.213352	-5.154102
C	11.327892	-10.589167	-2.472179
C	10.696388	-11.128803	-3.545300

C	12.054509	-8.693507	-1.021715
C	11.292870	-9.169252	-2.098283
C	13.830398	-19.004614	3.331186
O	14.807700	-19.261429	4.027863
O	12.602696	-19.406512	3.653460
C	9.018339	-21.142983	-1.737824
O	8.044546	-21.394609	-2.445382
O	9.451116	-22.058874	-0.823912
O	13.599262	-20.764211	1.214501
O	15.300417	-16.737225	4.488670
O	17.025777	-14.889047	4.818805
O	11.391740	-16.525756	1.388050
O	13.154526	-16.232878	3.474643
O	15.486512	-14.082344	1.233038
C	17.736535	-10.202602	7.020988
O	17.483995	-9.092255	7.486754
O	18.618179	-11.043668	7.634657
C	14.737364	-8.010970	3.286651
O	15.040515	-6.975344	2.736594
O	13.947857	-8.095740	4.383849
C	10.432260	-8.250697	-2.865225
O	9.795293	-8.490092	-3.878844
O	10.340466	-6.973234	-2.314204
C	10.052643	-12.360280	-6.254720
O	8.917963	-12.499523	-6.662262
O	10.912323	-11.416326	-6.710933
O	10.878986	-18.895225	-5.299909
O	9.155673	-14.988741	-3.099065
O	11.988968	-12.904887	-4.709851
O	10.159172	-12.934067	-1.436356
O	12.092739	-7.420203	-0.617988
O	11.945493	-11.481413	0.908939
O	15.945601	-9.441172	1.641270
O	13.829807	-11.928860	3.785575
H	9.895252	-17.807590	0.039643
H	11.589498	-21.421225	-0.333927
H	14.528975	-16.196391	0.337208
H	14.904086	-18.424761	1.622672
H	14.032714	-14.199953	4.293083
H	16.634329	-8.790840	5.032071
H	17.531409	-12.779508	6.327417
H	15.354906	-11.735846	0.763889
H	8.806473	-19.292545	-3.536880
H	8.901206	-17.085363	-4.448495
H	13.142668	-11.658627	-2.199945
H	13.902783	-8.008568	0.822382
H	11.098887	-14.767078	-7.264569
H	11.424987	-17.218635	-7.336338
H	10.120397	-10.509932	-4.223755
H	12.660703	-19.758565	4.574615
H	8.831359	-22.813062	-0.911188
H	13.337248	-21.660467	0.942046
H	15.295513	-17.714913	4.311152
H	17.781017	-14.370517	5.164658
H	18.900692	-10.579444	8.449492
H	13.707906	-7.181322	4.643177
H	9.450381	-6.621211	-2.562901
H	10.405431	-10.890441	-7.365649
H	11.256091	-19.205240	-6.144631
H	11.419981	-6.913124	-1.153525

C	10.511801	-16.688288	5.265182
C	7.768760	-16.110967	1.246720
C	8.519114	-11.275508	1.458153
C	11.307620	-11.852804	5.442396
N	8.319833	-13.736354	1.742468
N	9.143123	-16.025630	3.304700
N	10.659486	-14.220044	5.041929
N	9.834389	-11.939903	3.445121
C	11.181262	-13.206278	5.823125
C	10.834759	-15.399902	5.735204
C	9.790255	-16.959530	4.085530
C	8.561554	-16.704259	2.253285
C	10.745741	-11.307379	4.265804
C	9.486499	-11.040200	2.457196
C	7.887495	-12.523240	1.246112
C	7.552693	-14.714957	1.145557
C	11.635022	-13.761862	7.076988
C	11.430173	-15.114826	7.018952
C	9.642577	-18.265331	3.488280
C	8.897447	-18.108317	2.353432
C	6.533374	-14.091553	0.335921
C	6.736794	-12.739803	0.401891
C	11.036148	-9.995007	3.735648
C	10.261668	-9.830259	2.621342
H	12.031743	-13.188572	7.907811
H	11.635282	-15.848232	7.792137
H	10.088232	-19.182654	3.850546
H	8.632471	-18.885052	1.644821
H	5.745228	-14.617390	-0.192646
H	6.143303	-11.960233	-0.062676
H	11.785203	-9.316521	4.127124
H	10.268610	-8.985699	1.940762
C	11.015191	-17.850946	6.035594
C	12.383746	-17.980212	6.337809
C	10.157990	-18.890856	6.433118
H	13.074562	-17.201505	6.016922
H	9.090903	-18.804314	6.225938
C	12.885045	-19.113620	6.977430
C	10.643028	-20.026492	7.081985
H	13.950430	-19.214416	7.184652
H	9.953621	-20.817925	7.388070
C	12.012462	-20.144617	7.353976
C	7.221827	-16.956943	0.161057
C	6.658328	-18.234841	0.361961
C	7.313626	-16.501768	-1.168769
H	6.489183	-18.590106	1.378034
H	7.761083	-15.532023	-1.368401
C	6.299042	-19.046932	-0.711585
C	6.914137	-17.284901	-2.243645
H	5.880316	-20.039293	-0.537036
H	7.015397	-16.914664	-3.264416
C	6.456715	-18.588393	-2.029021
C	8.185563	-10.189482	0.506982
C	7.943830	-8.859218	0.903190
C	8.120049	-10.478226	-0.869074
H	7.937752	-8.613259	1.965014
H	8.344179	-11.484759	-1.213211
C	7.702564	-7.851554	-0.030475
C	7.838222	-9.491427	-1.805217
H	7.532737	-6.822524	0.286611

H	7.824071	-9.739406	-2.867177
C	7.663371	-8.170305	-1.390051
C	12.145226	-10.962213	6.278208
C	13.429859	-11.359585	6.690038
C	11.728042	-9.666206	6.641898
H	13.781852	-12.359386	6.441465
H	10.715071	-9.349149	6.392734
C	14.281169	-10.489095	7.358873
C	12.582370	-8.776073	7.287795
H	15.269156	-10.827577	7.664922
H	12.255192	-7.766090	7.537763
C	13.893494	-9.164044	7.600033
Zn	9.535460	-13.988759	3.356205
O	12.553697	-21.236647	7.984027
H	11.837108	-21.860626	8.196670
O	14.744922	-8.235262	8.124367
H	15.671748	-8.552862	8.020134
O	7.506843	-7.138401	-2.308249
H	7.453948	-7.544202	-3.195664
O	6.190889	-19.374477	-3.120823
H	6.543645	-20.272307	-2.927779

ZnTPPH

C	-0.071145	-1.445928	-3.040890
C	-0.136505	2.020293	0.425461
C	-0.136575	-1.446212	3.891966
C	-0.071216	-4.912563	0.425745
N	-0.102107	0.006430	1.878103
N	-0.132641	0.006004	-1.026951
N	-0.046306	-2.898060	-1.026387
N	-0.132699	-2.898623	1.877676
C	-0.110416	-4.262159	-0.822089
C	-0.110384	-2.693761	-2.390487
C	-0.042742	-0.198247	-2.389565
C	-0.072461	1.370060	-0.821329
C	-0.042824	-4.261239	1.673427
C	-0.072542	-2.693003	3.241734
C	-0.189116	-0.199440	3.240656
C	-0.189084	1.368985	1.672231
C	-0.246346	-4.933626	-2.095085
C	-0.246326	-3.966754	-3.061957
C	0.106891	1.074825	-3.058069
C	0.088042	2.041723	-2.091321
C	-0.364299	2.037358	2.942065
C	-0.364319	1.070397	3.909025
C	0.106770	-4.929746	2.946501
C	0.087922	-3.962998	3.913400
H	-0.356505	-6.004999	-2.229248
H	-0.356466	-4.100915	-4.133332
H	0.240011	1.208583	-4.126828
H	0.201493	3.113094	-2.222969
H	-0.501419	3.105995	3.072970
H	-0.501458	1.201306	4.977660
H	0.239866	-5.998508	3.080261
H	0.201350	-4.094649	4.984772
C	-0.060560	-1.445551	-4.528484
C	0.991389	-2.039830	-5.246668
C	-1.102525	-0.851810	-5.256761
H	1.814450	-2.497303	-4.696408
H	-1.933325	-0.394096	-4.718617

C	1.010297	-2.042297	-6.638744
C	-1.099616	-0.851696	-6.651202
H	1.834288	-2.494338	-7.191052
H	-1.927927	-0.395134	-7.199750
C	-0.040401	-1.447225	-7.347529
C	-0.148618	3.508007	0.425370
C	-1.192713	4.224639	-0.184292
C	0.883883	4.237702	1.033539
H	-2.008312	3.672848	-0.653149
H	1.708471	3.700430	1.503362
C	-1.213144	5.616731	-0.187923
C	0.879544	5.632210	1.032642
H	-2.031213	6.167953	-0.651919
H	1.700699	6.182069	1.500454
C	-0.171754	6.327001	0.421520
C	-0.148719	-1.446303	5.379679
C	-1.192838	-2.055950	6.096289
C	0.883776	-0.838149	6.109396
H	-2.008432	-2.524795	5.544481
H	1.708382	-0.368339	5.572141
C	-1.213298	-2.059581	7.488381
C	0.879407	-0.839047	7.503904
H	-2.031385	-2.523565	8.039586
H	1.700557	-0.371246	8.053780
C	-0.171914	-1.450154	8.198673
C	-0.060662	-6.400158	0.426122
C	0.991281	-7.118365	-0.168139
C	-1.102653	-7.128412	1.019847
H	1.814361	-6.568123	-0.625599
H	-1.933448	-6.590250	1.477547
C	1.010159	-8.510441	-0.170605
C	-1.099774	-8.522853	1.019962
H	1.834145	-9.062768	-0.622632
H	-1.928104	-9.071383	1.476511
C	-0.040564	-9.219204	0.424451
Zn	-0.103125	-1.446314	0.425359
O	0.020383	-1.476997	-8.717889
H	-0.769861	-1.032664	-9.072675
O	0.020191	-10.589565	0.394680
H	-0.770068	-10.944333	0.839001
O	-0.233690	-1.481902	9.569029
H	0.550317	-1.027585	9.924992
O	-0.233502	7.697359	0.389770
H	0.550507	8.053306	0.844099