

Electronic Supplementary Information

Blue-Green Emitting Cationic Iridium Complexes with 1,3,4-Oxadiazole Cyclometallating Ligands: Synthesis, Photophysical and Electrochemical Properties, Theoretical Investigation and Electroluminescent Devices

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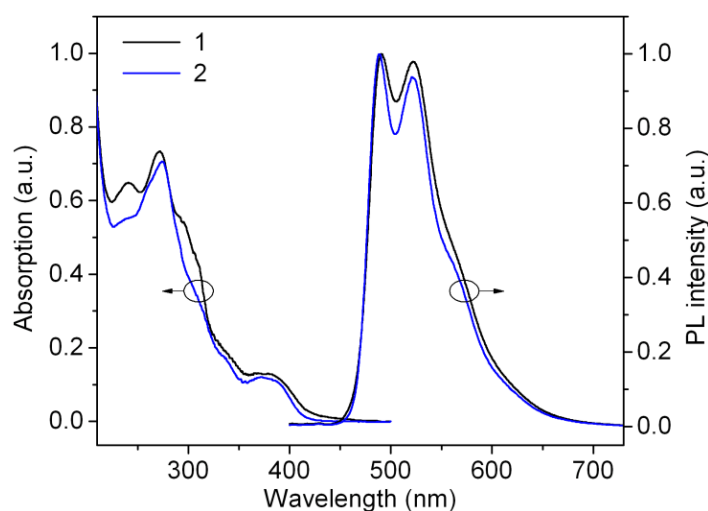


Figure S1. Comparison of the absorption and PL spectra for complexes 1 and 2 in CH₃CN solution

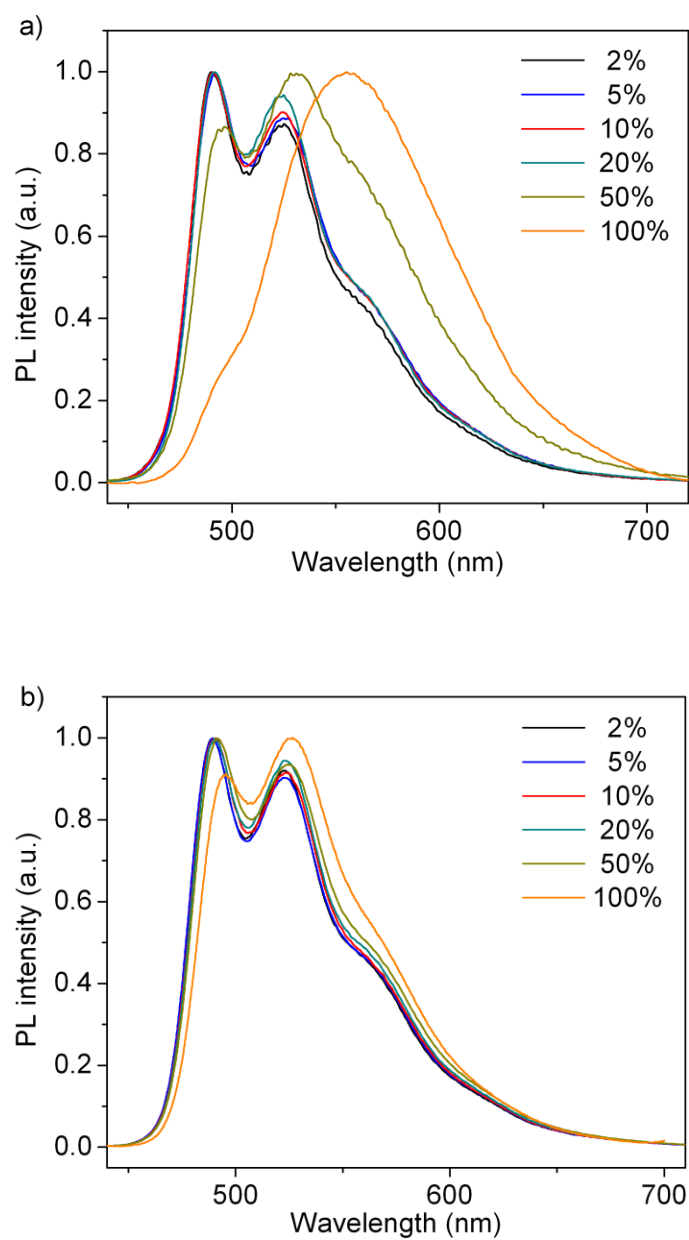


Figure S2. PL spectra of complexes 1 and 2 doped in PMMA with increasing doping concentrations.

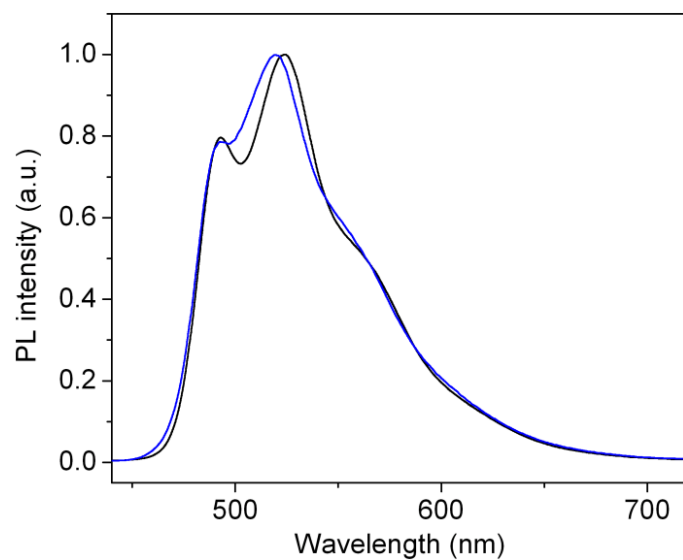


Figure S3. PL spectrum of the original powder of complex 1 (black) and PL spectrum of the powder of complex 1 (blue) produced by recrystallizing the ground powder from solution

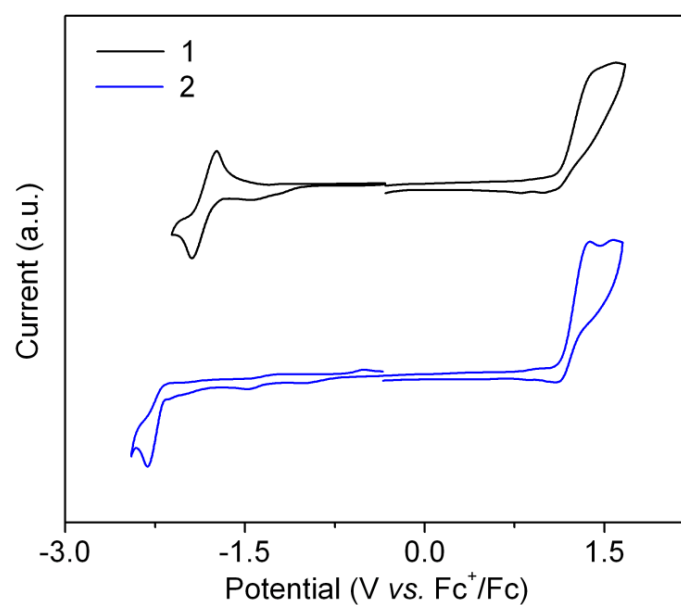


Figure S4. Cyclic voltammograms of complexes 1 and 2.

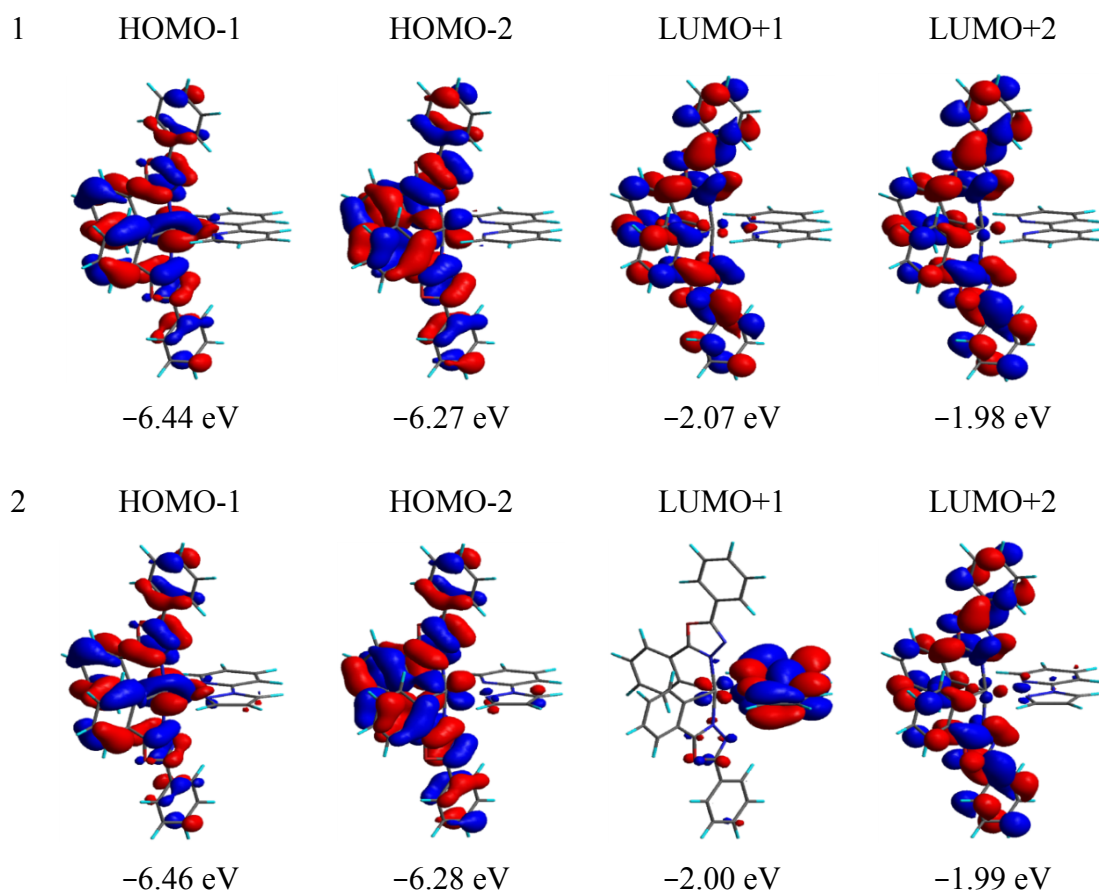


Figure S5. Distributions of HOMO-2, HOMO-1, LUMO+1 and LUMO+2 on complexes 1 and 2. The corresponding energy levels are also shown.

Table S1. Selected bond lengths (Å) and angles (degree) in the single crystal structure and ground state (S_0) calculated by DFT for complex 2.

	Metal-ligand bond lengths			Ligand bite angles	
	Ir-C(dph-oxd)	Ir-N(dph-oxd)	Ir-N(pzpy)	dph-oxd	pzpy
Crystal	2.027(5)	2.031(4)	2.129(3)	79.61(17)	75.92(16)
	2.033(4)	2.026(4)	2.096(5)	79.42(17)	
S_0 (DFT)	2.045	2.056	2.209	79.24	74.62
	2.047	2.055	2.170	79.22	

Table S2. The lowest triplet states of complexes 1 and 2 calculated from a TDDFT approach.

	State	$E[\text{eV}]^a$	Dominant excitations ^b	Nature
1	T ₁	2.70	H-2→L+1(11%), H-1→L+2 (29%), H→L+1 (40%)	dπ(Ir)-π(dph-oxd) → π*(dph-oxd)
	T ₂	2.72	H-2→L+2 (11%), H→L+2 (32%), H-1→L+1 (40%)	dπ(Ir)-π(dph-oxd) → π*(dph-oxd)
	T ₃	2.84	H→L (88%)	dπ(Ir)-π(dph-oxd) → π*(bpy)
2	T ₁	2.71	H-2→L (11%), H-1→L+2 (28%), H→L (42%)	dπ(Ir)-π(dph-oxd) → π*(dph-oxd)
	T ₂	2.73	H-2→L+2 (10%), H→L+2 (31%), H-1→L (38%)	dπ(Ir)-π(dph-oxd) → π*(dph-oxd)
	T ₃	3.10	H-1→L+5 (10%), H-2→L (13%), H→L (15%), H-2→L+4 (23%)	dπ(Ir)-π(dph-oxd) → π*(dph-oxd)
	T ₇	3.27	H→L+1 (70%)	dπ(Ir)-π(dph-oxd) → π*(pzpy)

^a Vertical excitation energies. ^b Dominant monoexcitations with contributions (within parentheses) greater than 10%; H and L denote HOMO and LUMO, respectively.

Table S3. Cartesian coordinates of all the optimized geometries of complexes 1 and 2.

Complex 1

	S ₀			T ₁		
Ir	-0.000085	-0.110259	-0.000138	0.021078	-0.141430	0.017666
C	0.158733	-1.573275	1.427188	-0.156998	-1.598428	-1.413099
N	2.041695	-0.260807	0.173005	-2.038066	-0.255456	-0.170873
N	-2.041819	-0.260801	-0.173108	2.010956	-0.289590	0.161441
C	-0.159050	-1.573550	-1.427149	0.136452	-1.600472	1.433265
N	3.134594	0.345902	-0.400282	-3.128123	0.376059	0.379340
N	-3.134619	0.346085	0.400158	3.051721	0.320506	-0.367283
O	-3.796047	-1.167252	-1.088803	3.825034	-1.252166	1.067798
O	3.795780	-1.167159	1.089068	-3.791753	-1.136502	-1.109510
C	-0.857918	-2.254012	2.113124	0.856247	-2.290052	-2.090545

C	-0.560518	-3.214125	3.087398	0.551780	-3.247701	-3.064988
C	0.763715	-3.534023	3.414760	-0.774548	-3.550831	-3.398144
C	1.805289	-2.881744	2.763689	-1.811628	-2.884922	-2.753593
C	1.494866	-1.921164	1.790736	-1.495694	-1.926736	-1.780384
C	2.452917	-1.151145	1.050331	-2.450363	-1.143266	-1.048975
C	4.169790	-0.213770	0.164086	-4.164064	-0.169633	-0.197450
C	5.583650	0.041494	-0.060617	-5.576379	0.111919	0.002915
C	6.561256	-0.671131	0.653339	-6.554968	-0.587997	-0.722194
C	7.910918	-0.412356	0.423516	-7.903142	-0.303265	-0.515889
C	8.293013	0.551605	-0.512969	-8.282469	0.673979	0.407884
C	7.319808	1.261477	-1.224266	-7.308193	1.371169	1.130185
C	5.969054	1.011454	-1.002959	-5.958872	1.095276	0.932489
C	0.857560	-2.254496	-2.112956	-0.882618	-2.257143	2.110351
C	0.560091	-3.214931	-3.086876	-0.612096	-3.238048	3.084707
C	-0.764177	-3.534937	-3.414037	0.725430	-3.597002	3.398900
C	-1.805703	-2.882437	-2.763126	1.786197	-2.992401	2.767062
C	-1.495208	-1.921533	-1.790508	1.520874	-1.983750	1.779747
C	-2.453173	-1.151316	-1.050206	2.447732	-1.267779	1.067039
C	-4.169906	-0.213643	-0.163992	4.139572	-0.247031	0.164415
C	-5.583728	0.041773	0.060781	5.505124	0.072990	-0.103816
C	-6.561428	-0.669660	-0.654233	6.546155	-0.628208	0.549588
C	-7.911049	-0.410698	-0.424385	7.870901	-0.308090	0.279602
C	-8.293013	0.552283	0.513161	8.181848	0.704923	-0.635719
C	-7.319714	1.260968	1.225515	7.154020	1.403455	-1.286390
C	-5.969001	1.010731	1.004209	5.826180	1.097087	-1.028738
N	-0.022765	1.616015	1.340978	0.061849	1.618302	-1.297806
C	-0.024657	2.834108	0.740061	0.079934	2.823998	-0.673608
C	-0.076145	4.005039	1.502865	0.147232	4.007679	-1.415222
C	-0.122862	3.920570	2.891432	0.191248	3.947526	-2.805286

C	-0.119863	2.664589	3.494327	0.169131	2.703425	-3.431655
C	-0.070495	1.537212	2.681309	0.106282	1.562285	-2.638860
H	-1.899658	-2.037014	1.896272	1.898818	-2.085122	-1.867410
H	-1.373563	-3.722009	3.599501	1.361121	-3.766232	-3.571855
H	0.975939	-4.282281	4.171528	-0.992412	-4.297201	-4.155049
H	2.840670	-3.106276	3.002402	-2.848287	-3.097184	-2.997203
H	6.264926	-1.419501	1.380062	-6.260665	-1.346553	-1.439099
H	8.664279	-0.964391	0.976407	-8.657488	-0.845350	-1.077169
H	9.345810	0.749836	-0.688845	-9.334165	0.892464	0.565324
H	7.614959	2.010543	-1.952163	-7.601402	2.130471	1.848157
H	5.209687	1.558325	-1.551288	-5.198576	1.632164	1.489318
H	1.899309	-2.037382	-1.896248	-1.918781	-2.011980	1.895596
H	1.373084	-3.723004	-3.598873	-1.432158	-3.727503	3.600732
H	-0.976441	-4.283463	-4.170528	0.909609	-4.359473	4.150294
H	-2.841101	-3.107012	-3.001721	2.811031	-3.259437	3.003426
H	-6.265200	-1.417233	-1.381818	6.302970	-1.411989	1.257944
H	-8.664483	-0.961802	-0.978107	8.666672	-0.848231	0.782729
H	-9.345779	0.750667	0.689050	9.218930	0.950128	-0.842031
H	-7.614763	2.009245	1.954263	7.396228	2.188506	-1.995702
H	-5.209563	1.556638	1.553401	5.027197	1.633561	-1.528385
H	-0.084146	4.975318	1.023859	0.169124	4.969260	-0.919488
H	-0.162876	4.824206	3.490002	0.243647	4.861397	-3.387115
H	-0.156842	2.550397	4.571348	0.202661	2.608649	-4.510625
H	-0.071959	0.537278	3.097847	0.094326	0.570142	-3.074003
C	0.025446	2.834068	-0.740420	0.022895	2.800717	0.807642
C	0.077288	4.004946	-1.503269	-0.017688	3.960068	1.588479
C	0.123896	3.920394	-2.891841	-0.076594	3.853955	2.975383
H	0.085665	4.975232	-1.024293	-0.008412	4.937947	1.125444
C	0.070801	1.537073	-2.681595	-0.060832	1.474272	2.729800

C	0.120479	2.664388	-3.494689	-0.098665	2.589421	3.559953
H	0.164142	4.823987	-3.490456	-0.107998	4.748951	3.587319
H	0.071980	0.537117	-3.098090	-0.086752	0.466207	3.126999
H	0.157329	2.550114	-4.571699	-0.146622	2.460180	4.634792
N	0.023131	1.615940	-1.341281	0.002459	1.575520	1.392519

Complex 1

	T ₃			
Ir	0.000000	0.203493	0.000000	
C	-0.205112	1.590013	1.462096	
N	-2.046015	0.307591	0.111055	
N	2.046015	0.307591	-0.111055	
C	0.205112	1.590013	-1.462096	
N	-3.102020	-0.324188	-0.487180	
N	3.102020	-0.324188	0.487179	
O	3.832867	1.095697	-1.063358	
O	-3.832867	1.095697	1.063358	
C	0.798170	2.267432	2.181511	
C	0.468848	3.191113	3.172360	
C	-0.871730	3.471856	3.483950	
C	-1.901048	2.821054	2.804225	
C	-1.564472	1.893250	1.817059	
C	-2.494838	1.138255	1.028271	
C	-4.164688	0.167256	0.097419	
C	-5.562144	-0.138043	-0.146366	
C	-6.572768	0.503661	0.589889	
C	-7.907594	0.195358	0.340280	
C	-8.240707	-0.747023	-0.636647	
C	-7.234575	-1.385958	-1.369434	

C	-5.897622	-1.086575	-1.129670
C	-0.798170	2.267432	-2.181511
C	-0.468848	3.191113	-3.172360
C	0.871730	3.471857	-3.483950
C	1.901048	2.821054	-2.804225
C	1.564472	1.893251	-1.817059
C	2.494838	1.138255	-1.028271
C	4.164688	0.167256	-0.097419
C	5.562144	-0.138043	0.146366
C	6.572768	0.503661	-0.589889
C	7.907594	0.195358	-0.340280
C	8.240707	-0.747023	0.636647
C	7.234575	-1.385958	1.369434
C	5.897622	-1.086576	1.129670
N	-0.076257	-1.500809	1.341405
C	-0.037369	-2.744240	0.709866
C	-0.086041	-3.920679	1.513764
C	-0.186653	-3.835633	2.879793
C	-0.239885	-2.556469	3.496987
C	-0.183066	-1.440771	2.689304
H	1.843874	2.066526	1.973688
H	1.258955	3.702650	3.713466
H	-1.108389	4.193859	4.258270
H	-2.940263	3.028914	3.037132
H	-6.313132	1.234300	1.347882
H	-8.687960	0.690744	0.908777
H	-9.282829	-0.984022	-0.827214
H	-7.493651	-2.117749	-2.127698
H	-5.111705	-1.577480	-1.693134

H	-1.843874	2.066526	-1.973688
H	-1.258955	3.702650	-3.713466
H	1.108389	4.193859	-4.258270
H	2.940263	3.028914	-3.037132
H	6.313132	1.234300	-1.347882
H	8.687960	0.690744	-0.908777
H	9.282829	-0.984022	0.827214
H	7.493651	-2.117749	2.127698
H	5.111705	-1.577480	1.693134
H	-0.046043	-4.892107	1.035595
H	-0.223499	-4.738284	3.481468
H	-0.312630	-2.443338	4.572010
H	-0.208500	-0.445378	3.117163
C	0.037369	-2.744240	-0.709866
C	0.086041	-3.920679	-1.513764
C	0.186653	-3.835633	-2.879793
H	0.046043	-4.892107	-1.035595
C	0.183066	-1.440771	-2.689304
C	0.239885	-2.556469	-3.496987
H	0.223499	-4.738284	-3.481468
H	0.208500	-0.445378	-3.117163
H	0.312630	-2.443338	-4.572010
N	0.076257	-1.500808	-1.341405

Complex 2

	S ₀			T ₁		
Ir	0.000142	-0.087520	-0.042273	-0.024633	-0.117109	-0.064010
C	0.168205	-1.214259	1.656713	0.148752	-1.268346	1.617333

N	2.044716	-0.198348	0.143924	2.036092	-0.200351	0.138874
N	-2.044072	-0.261956	-0.169426	-2.017033	-0.280325	-0.168262
C	-0.169911	-1.806492	-1.140216	-0.152738	-1.811903	-1.180167
N	3.134080	0.281547	-0.544550	3.128467	0.317361	-0.515707
N	-3.132797	0.451512	0.274009	-3.052276	0.424387	0.237692
O	-3.803601	-1.319493	-0.891486	-3.838282	-1.389136	-0.869271
O	3.803503	-0.890508	1.222796	3.785508	-0.890127	1.232381
C	-0.845263	-1.729542	2.477447	-0.867316	-1.807721	2.416914
C	-0.543101	-2.467443	3.628061	-0.566879	-2.565777	3.554767
C	0.782526	-2.720684	4.003847	0.758087	-2.813394	3.935040
C	1.821219	-2.223836	3.223684	1.798139	-2.291465	3.173126
C	1.506403	-1.485039	2.074594	1.486425	-1.532560	2.036686
C	2.460802	-0.887052	1.185056	2.444591	-0.907403	1.169660
C	4.172364	-0.146413	0.120487	4.161937	-0.111041	0.156813
C	5.584785	0.063477	-0.154403	5.575283	0.126849	-0.087717
C	6.566451	-0.486431	0.686560	6.550233	-0.428417	0.757556
C	7.914505	-0.272625	0.406608	7.899496	-0.188242	0.506558
C	8.290534	0.485122	-0.705457	8.283085	0.601284	-0.580531
C	7.313216	1.032580	-1.543410	7.312371	1.154257	-1.422560
C	5.964012	0.825557	-1.273658	5.961991	0.920990	-1.181855
C	0.843744	-2.615728	-1.671610	0.863419	-2.579265	-1.731175
C	0.541184	-3.749012	-2.435209	0.587141	-3.722427	-2.506694
C	-0.784661	-4.118397	-2.697617	-0.752051	-4.133048	-2.740164
C	-1.822881	-3.342603	-2.193593	-1.809491	-3.422483	-2.223629
C	-1.507824	-2.209848	-1.429720	-1.539007	-2.249121	-1.441088
C	-2.460856	-1.303871	-0.856037	-2.460881	-1.411000	-0.869247
C	-4.171580	-0.201889	-0.170425	-4.145202	-0.229005	-0.172769
C	-5.583956	0.098298	0.001821	-5.507805	0.141084	0.038281
C	-6.565385	-0.730412	-0.566817	-6.555499	-0.668563	-0.461162

C	-7.913546	-0.426947	-0.388906	-7.877367	-0.299447	-0.245178
C	-8.289974	0.696527	0.351612	-8.179090	0.869945	0.463653
C	-7.312912	1.522191	0.917874	-7.144714	1.676900	0.960255
C	-5.963578	1.228893	0.746742	-5.819663	1.323541	0.754044
N	0.001250	1.913396	0.894232	-0.037211	1.896976	0.875089
C	-0.003086	2.962642	0.050148	-0.031196	2.944496	0.029966
C	-0.024961	4.286127	0.490690	-0.058424	4.268270	0.469198
C	-0.041683	4.519732	1.861288	-0.090956	4.502261	1.839554
C	-0.038600	3.438331	2.744421	-0.098161	3.421786	2.723769
C	-0.017707	2.153871	2.220270	-0.072019	2.137024	2.200474
N	0.012329	2.635247	-1.320742	0.002315	2.617838	-1.341850
N	0.000623	1.320521	-1.693052	-0.009911	1.304920	-1.719122
C	0.022265	1.306274	-3.021282	0.035661	1.293458	-3.046963
C	0.048654	2.622509	-3.529974	0.076149	2.610290	-3.550752
C	0.042493	3.442466	-2.425038	0.054512	3.427142	-2.442921
H	-1.887668	-1.555163	2.228760	-1.908777	-1.638146	2.162515
H	-1.353665	-2.852484	4.241136	-1.378528	-2.970562	4.153170
H	0.998218	-3.296973	4.897703	0.972820	-3.405066	4.818916
H	2.857616	-2.399314	3.496405	2.833927	-2.462998	3.450024
H	6.274367	-1.074644	1.549480	6.252253	-1.041204	1.601134
H	8.671398	-0.698372	1.057600	8.651369	-0.618179	1.160570
H	9.342147	0.649149	-0.919588	9.335644	0.785753	-0.772154
H	7.603983	1.621322	-2.407628	7.609237	1.767501	-2.267419
H	5.200878	1.246870	-1.919002	5.203992	1.345941	-1.830833
H	1.886133	-2.366329	-1.499422	1.900210	-2.297701	-1.573478
H	1.351670	-4.354329	-2.832545	1.404301	-4.298189	-2.929847
H	-1.000478	-5.000887	-3.291128	-0.940039	-5.020847	-3.337107
H	-2.859369	-3.603054	-2.386386	-2.835603	-3.728020	-2.399991
H	-6.272925	-1.602231	-1.141561	-6.319628	-1.573446	-1.009601

H	-8.670189	-1.068592	-0.829050	-8.678226	-0.923201	-0.629476
H	-9.341674	0.928898	0.487878	-9.214012	1.152441	0.628899
H	-7.604012	2.394990	1.493656	-7.379602	2.583091	1.509586
H	-5.200667	1.864105	1.183578	-5.015809	1.942772	1.136325
H	-0.030411	5.109921	-0.210707	-0.056286	5.092072	-0.232185
H	-0.058655	5.538520	2.232553	-0.112343	5.521301	2.209885
H	-0.053077	3.582853	3.817887	-0.124997	3.567283	3.796823
H	-0.017834	1.276258	2.854965	-0.080051	1.259760	2.835887
H	0.020225	0.363539	-3.548229	0.041338	0.351232	-3.575069
H	0.070484	2.927760	-4.564328	0.117110	2.918859	-4.583524
H	0.059104	4.517336	-2.345526	0.074622	4.501740	-2.360560