Electronic Supplementary Information (ESI)

Atomically precise and monolayer protected iridium clusters in solution

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Content list

Supplementary Information 1

Instrumentation:

UV-Vis spectral measurements on the cluster were performed using a Perkin Elmer Lambda 25 instrument in the range of 200-1100 nm. Photoluminescence spectra of samples were measured with a Jobin Vyon NanoLog instrument. Matrix-assisted desorption ionization mass spectrometric (MALDI MS) measurements were carried out using a Voyager-DE PRO Biospectrometry Workstation from Applied Biosystems. DHB and other matrices listed in the text were used in the ratio of 1:100 of sample:matrix. A pulsed nitrogen laser of wavelength 337 nm was used for the MALDI MS measurements. Mass spectra were collected in linear positive ion mode and were averaged for 250 shots. High resolution transmission electron microscopy of cluster was conducted with a JEOL 3010 instrument. The samples for TEM were prepared by drop casting THF solution of cluster on carbon-coated copper grids and allowing it to dry under ambient conditions. FT-IR spectra were taken using a Perkin Elmer Spectrum One spectrometer. X-ray photoelectron spectroscopic (XPS) measurements were carried out with an Omicron ESCA Probe spectrometer using polychromatic MgKα X-rays (hυ = 1253.6 eV). The THF solution of sample was drop casted on a sample stub and dried, several times to form a thin film. The measurements were conducted with constant analyzer energy of 20 eV. Powder XRD of Ir_9PET_6 cluster was recorded by PANalytical X'pertPro diffractometer. The sample for XRD was prepared on a glass slide and diffractogram was collected for 2 theta range of 5 to 100 degrees with Cu Kα radiation. Small Angle X-ray Scattering (SAXS) analysis on cluster solution was done using Rigaku Smart Lab X-ray Diffractometer operating at 9 kW (Cu-Kα radiation; λ = 1.54059 Å). The cluster solution was filled inside a borosilicate capillary tube of internal diameter approximately 1.5 mm. The raw SAXS profiles were solved using NANO-Solver programme (Rigaku). Prior to fittings the raw data was corrected for background absorption and air scattering. The 'corrected' raw profile was fitted with 'sphere' as well as 'core – shell' models to evaluate the best suited model for the Ir_9PET_6 sample. The densities of PET ligand (1.03 g/cm^3), toluene (0.87 g/cm^3) and Ir (22.56 g/cm^3) have been used to fit these profiles.

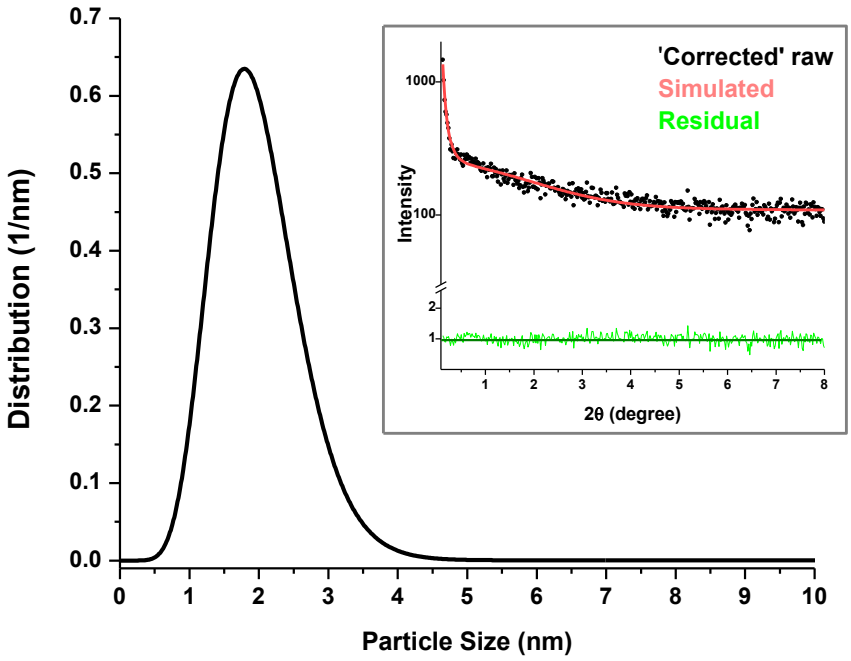

Fig. S1. Particle size distribution curve of Ir_9PET_6 evaluated using 'sphere' model. The corrected raw, simulated and residual SAXS profiles are shown in the inset.

Table S1: SAXS parameters for Ir@PET solution in toluene.

Model	Avg. size (nm)	Vol (%)	Normalized dispersion (σ)	Shell diameter (nm)	Avg. metal cluster core size (nm)	R-esidual factor
Core-shell	2.0	98.08 (rest are bigger particles)	0.317	0.4	1.6	1.94
Sphere	1.99	95.04 (rest are bigger particles)	0.314	--	--	1.93

Supplementary Information 2

UV/Vis spectra and photographs of samples synthesized using varying thiol concentrations

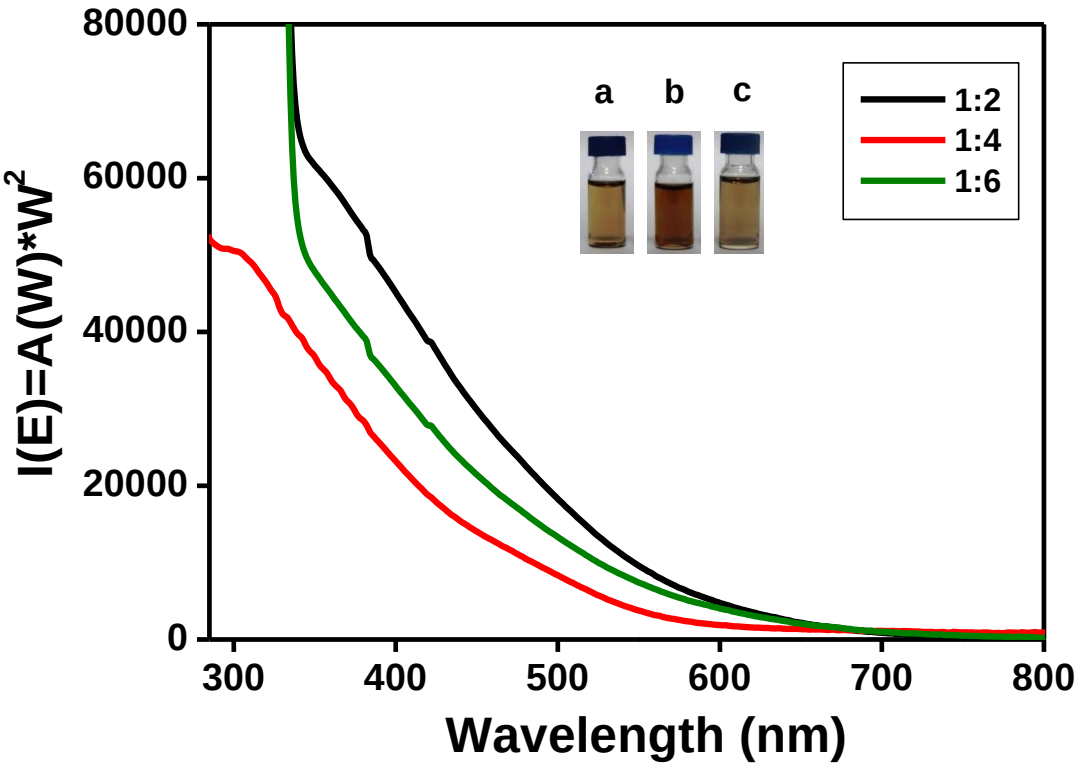

Fig. S2. UV/Vis spectra of samples synthesized using metal to thiol molar ratio of 1:2, 1:4 and 1:6. Inset shows the photographs (a-1:2, b-1:4 and c-1:6) samples. It is clearly seen that the sample 'b' corresponding to 1:4 ratio has intense color and this ratio works out better giving good yield. It also has absorption features different from other two compositions.

Supplementary Information 3

XPS survey spectrum of Ir_9PET_6 cluster

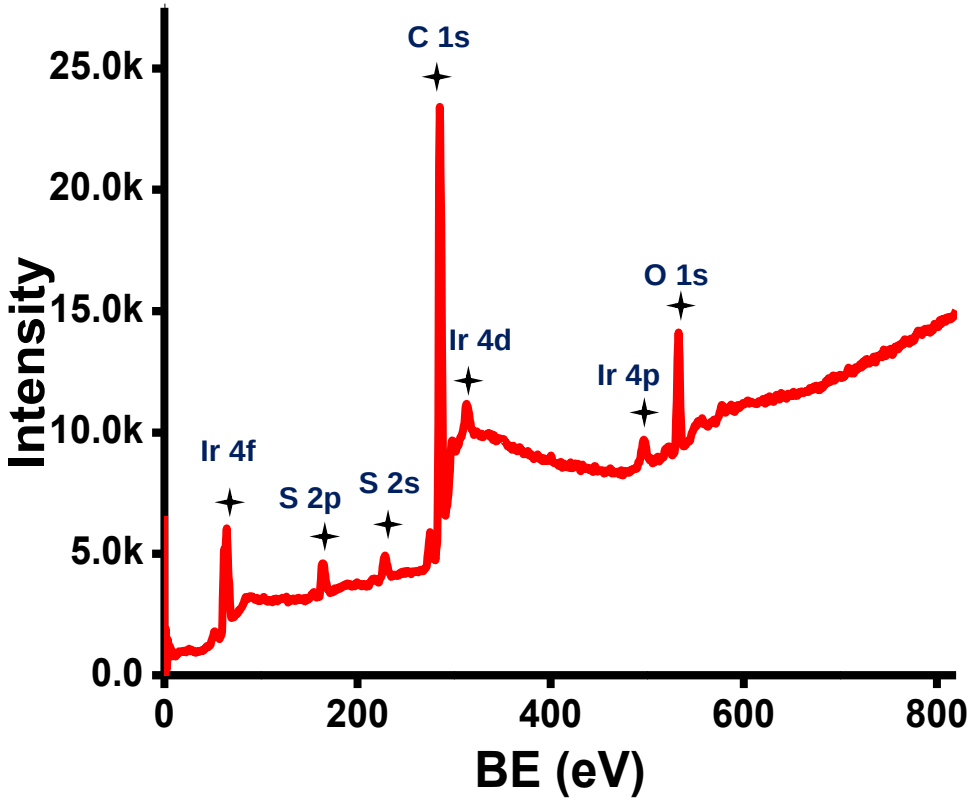

Fig. S3. XPS survey spectrum of Ir_9PET_6 measured from 0 – 1000 eV showing the elements Ir, S, C and O.

Supplementary Information 4

Expanded view of NMR spectrum of Ir_9PET_6 cluster as compared to that of free PET

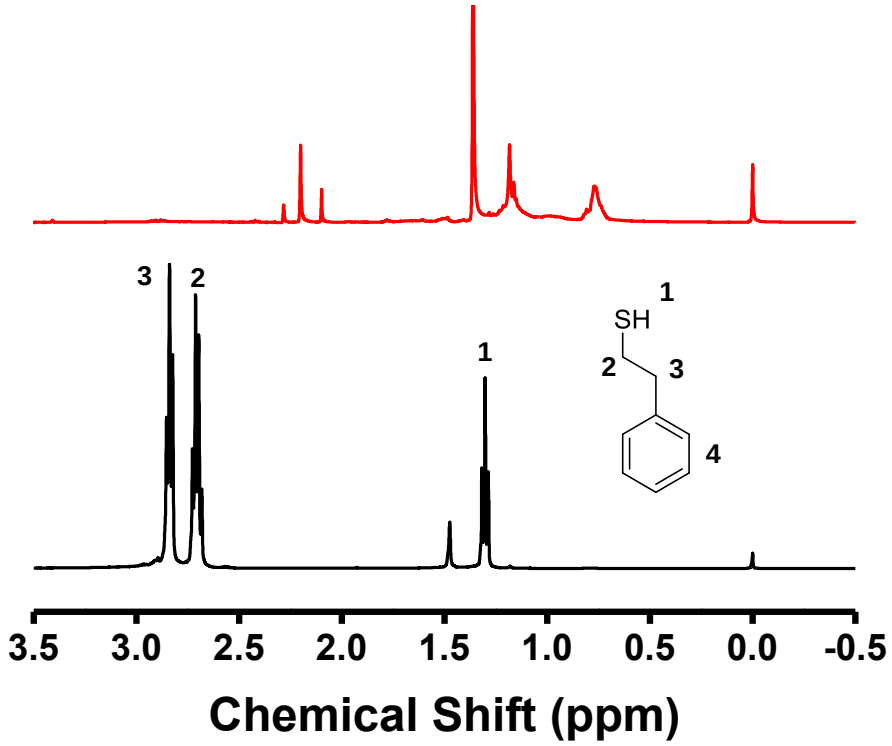

Fig. S4. Expanded view of comparative plot of NMR spectra of Ir_9PET_6 clusters (red trace) and PET (black trace).

Supplementary Information 5

XRD pattern of Ir_9PET_6 cluster

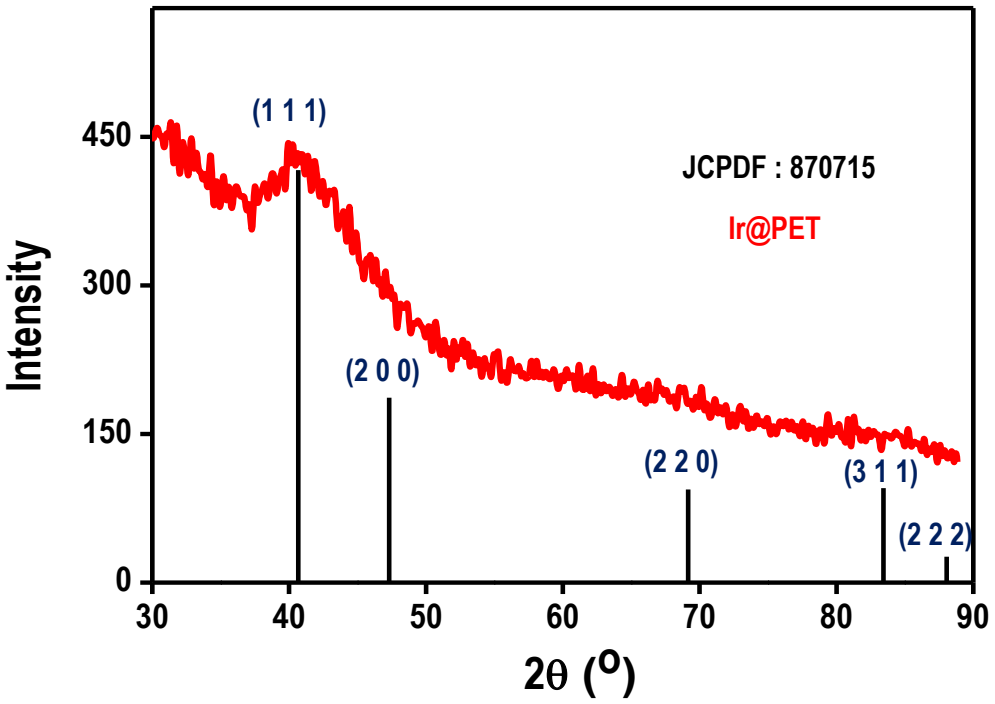

Fig. S5. Powder XRD pattern of Ir_9PET_6 clusters measured by drop casting THF solution of clusters on a glass slide several times and drying to form a thin film. Standard pattern of Ir metal is also shown.

Supplementary Information 6

Mass spectra obtained using different matrices

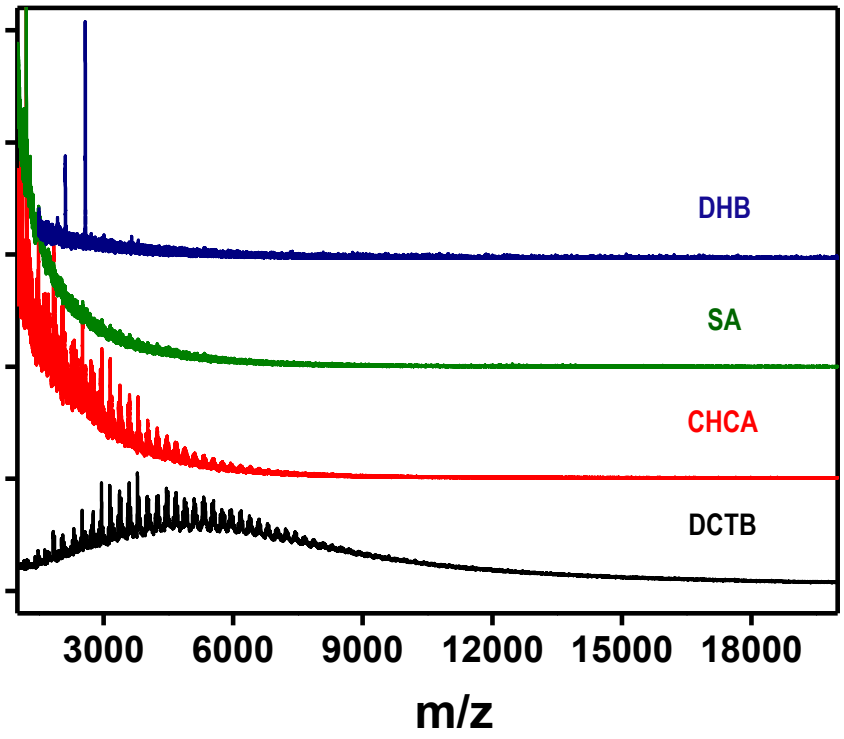

Fig. S6. MALDI MS obtained using different matrices are plotted together for comparison. The matrix used to obtain each spectrum is indicated in the figure.

Supplementary Information 7

Mass spectrum at threshold laser intensity

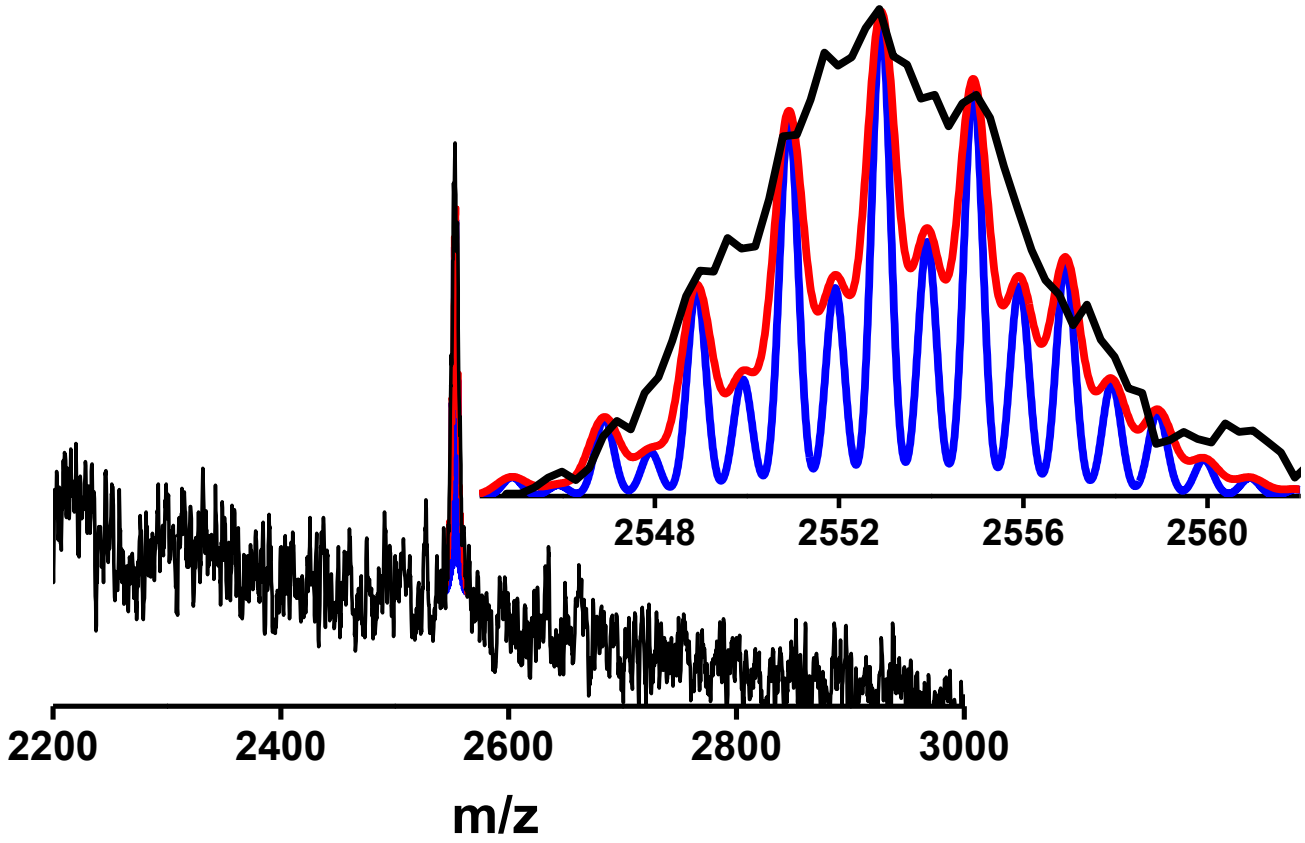

Fig. S7. MALDI MS obtained at threshold laser intensity showing better resolution. Inset shows the expanded view, wherein, it can be seen that experimental spectrum (black trace) is in better agreement with the theoretical spectrum calculated at similar resolution (red trace) and blue trace is the theoretical spectrum calculated at highest possible resolution. The experimental spectrum has more noise due to poor signal quality.

Supplementary information 8

Time dependent UV/Vis spectra

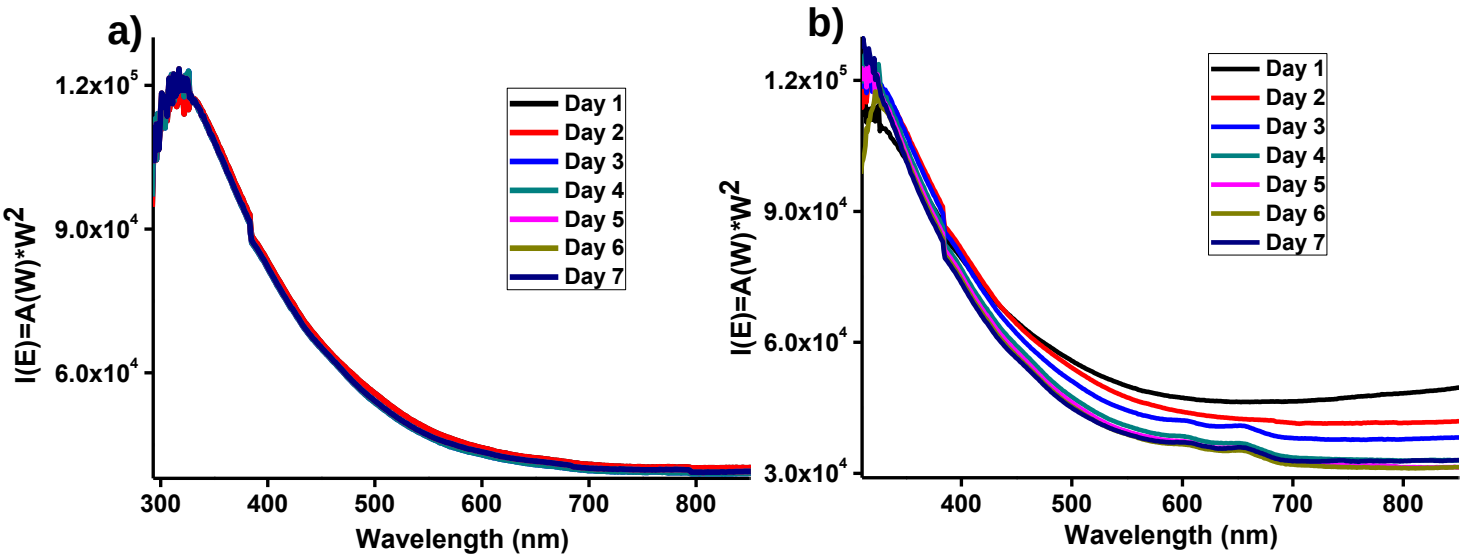

Fig. S8. Time dependent UV/Vis spectra of the cluster solution in THF kept a) in fridge (at ~ 4 ^{o}C) and b) at room temperature measured for a time period of 7 days.

Supplementary Information 9

Atomic coordinates of optimized geometries of model clusters:

1. $Ir_3(SCH_3)_2$ – isomer (a)

Ir	11.623303	12.849419	13.136886
S	12.599564	12.455964	11.255281
Ir	14.751456	12.446011	11.530630
Ir	14.902190	11.633294	13.683341
S	13.188610	12.599242	14.598317
C	12.143934	10.732869	10.744433
H	12.589926	10.548600	9.759417
H	11.050211	10.680447	10.687162
H	12.525054	10.021048	11.481836
C	13.761688	14.292242	15.091198
H	14.184926	14.801766	14.221130
H	12.892324	14.839939	15.473881
H	14.517185	14.172468	15.877300

2. $Ir_3(SCH_3)_2$ – isomer (b)

C	12.755526	10.649612	11.526901
S	12.311646	12.310260	10.849593
Ir	14.121808	13.459329	10.639438
Ir	13.397168	14.101478	12.798571
S	14.441620	14.602178	14.612887
C	15.017882	13.109171	15.525506
Ir	11.190566	13.373750	12.350818

H	13.378101	10.146656	10.777789
H	11.820013	10.101180	11.687424
H	13.300330	10.777569	12.466462
H	15.535240	13.454702	16.429947
H	14.160506	12.488027	15.804834
H	15.709442	12.533683	14.901403

3. $Ir_3(SCH_3)_2$ – isomer (c)

C	12.053627	10.753478	10.639916
S	12.644522	12.490833	11.106043
Ir	11.712954	12.651744	13.132928
Ir	14.092210	11.849749	13.695775
S	10.041237	13.068855	14.439584
C	10.157745	14.878418	14.956478
Ir	14.792378	12.224427	11.369537
H	12.113242	10.702989	9.551796
H	11.021295	10.658932	10.964896
H	12.679660	10.019020	11.109310
H	9.703707	14.957657	15.942446
H	11.195730	15.189908	15.033705
H	9.613137	15.490931	14.246902

4. $Ir_3(SCH_3)_2$ – isomer (d)

Ir	6.563522	7.035119	6.692346
Ir	8.957637	7.246990	7.375922

Ir	6.920398	8.565528	8.474533
S	8.449089	7.455616	9.603860
S	8.195623	7.260862	5.204826
C	8.154369	8.956055	4.508244
H	7.368388	9.005523	3.746746
H	9.133699	9.145599	4.051649
H	7.964161	9.675912	5.311083
C	7.715083	5.893616	10.232591
H	7.066706	6.125718	11.083994
H	7.147821	5.408341	9.430838
H	8.546625	5.252550	10.550354

5. $Ir_3(SCH_3)_2$ – isomer (e)

Ir	1.112160	-1.002094	0.239234
Ir	0.023392	1.146970	-0.028114
Ir	-1.226476	-0.988150	-0.260257
S	-2.224277	1.158037	-0.391473
S	2.237681	1.157422	0.387517
C	3.190393	1.429044	-1.166390
H	4.178463	0.971512	-1.041434
H	3.297747	2.509234	-1.314400
H	2.668594	0.983663	-2.016962
C	-3.115733	1.511332	1.182430
H	-4.111855	1.059778	1.115313
H	-2.565060	1.096467	2.030148

H	-3.205560	2.598555	1.284952

6. $Ir_3(SCH_3)_2$ – isomer (f)

Ir	12.309177	12.706316	12.742232
S	13.231746	12.738223	14.715847
Ir	15.206540	11.993012	13.957759
Ir	14.474419	13.072322	11.896811
S	16.277440	11.718008	11.939570
C	13.347819	14.487820	15.294727
H	13.955881	15.058931	14.586622
H	13.835534	14.461422	16.276810
H	12.341128	14.909298	15.374398
C	15.995190	10.122416	11.089021
H	16.753601	9.414767	11.444410
H	16.101914	10.278673	10.010157
H	14.992759	9.755255	11.327740

7. $Ir_3(SCH_3)_2$ – isomer (g)

Ir	0.003767	1.611685	0.008810
Ir	1.064370	-0.450027	0.601114
Ir	-1.049128	-0.450795	-0.591141
S	-3.022318	-1.181875	-0.121888
S	3.039527	-1.174103	0.129848
C	3.481962	-0.942535	-1.626974
C	-3.465241	-0.955243	1.635446
H	-2.758908	-1.501862	2.267970
H	-3.445397	0.111429	1.881163
H	-4.478574	-1.352137	1.772083
H	3.461694	0.124830	-1.869679
H	2.775733	-1.487632	-2.260911
H	4.495450	-1.338612	-1.764838

8. $Ir_3(SCH_3)_2$ – isomer (h)

Ir	-0.725569	1.187585	-0.155868
Ir	1.289216	0.016141	0.512233
Ir	-0.713040	-1.200389	-0.111513
S	-2.639575	-0.025935	-0.639521
S	3.430989	0.018315	0.023562
C	3.641983	-0.014594	-1.795866
C	-3.724016	-0.003824	0.852113
H	-3.123551	0.016062	1.764779
H	-4.356171	0.889236	0.794654
H	-4.347114	-0.904734	0.827792
H	3.181242	0.871374	-2.242936
H	3.191679	-0.922019	-2.209272
H	4.720699	-0.012054	-1.994663

9. $Ir_3(SCH_3)_2$ – isomer (i)

Ir	-1.018558	-0.086384	0.203833
Ir	1.388298	0.885978	0.091153
Ir	0.964000	-1.411057	-0.135851
S	-0.393618	1.824729	-0.817694
S	-3.111925	-0.569354	0.545695
C	-4.143636	-0.424737	-0.964817
C	-0.937631	3.312110	0.138787
H	-0.433650	4.186603	-0.291032
H	-0.702417	3.207804	1.201129

H	-2.021844	3.405736	0.001339
H	-3.840402	0.449371	-1.549994
H	-4.022079	-1.329692	-1.570819
H	-5.191764	-0.329382	-0.655038

10. $Ir_3(PET)_1$ – isomer (j)

Ir	11.078616	6.678504	18.087445
Ir	9.566682	7.838141	16.705897
Ir	10.806959	7.662714	14.711221
S	12.179877	6.878933	16.216417
C	13.396818	8.259880	16.522600
C	14.187628	8.574787	15.248172
C	15.199424	9.673517	15.475276
C	14.802121	11.018794	15.475887
C	15.726910	12.037352	15.707052
C	17.068400	11.726818	15.942793
C	17.476600	10.392005	15.943750
C	16.548086	9.374938	15.712194
H	14.050443	7.893825	17.327328
H	12.833058	9.126431	16.884590
H	14.693232	7.666017	14.889255
H	13.468818	8.879584	14.468340
H	16.875840	8.333336	15.707147
H	18.522677	10.140136	16.120841
H	17.792669	12.521972	16.120083

H	15.400257	13.077620	15.698158
H	13.756508	11.269285	15.285638

11. $Ir_3(PET)_1$ – isomer (k)

C	-1.113381	1.205743	0.063229
C	-2.443906	1.237395	-0.357267
C	-3.167140	0.049573	-0.483394
C	-2.551710	-1.167655	-0.184217
C	-1.220986	-1.194809	0.235942
C	-0.483474	-0.009632	0.365635
C	0.967652	-0.044434	0.786471
C	1.891885	-0.175121	-0.431508
S	3.653687	-0.216915	0.092567
Ir	5.031883	-0.397786	-1.565437
Ir	4.876410	-1.717521	-3.542161
H	-0.555645	2.138919	0.166062
H	-2.918517	2.192875	-0.582606
H	-4.207328	0.072801	-0.808569
H	-3.110923	-2.099450	-0.273748
H	-0.747892	-2.149637	0.474593
H	1.777682	0.673856	-1.117270
H	1.697121	-1.100549	-0.988036
H	1.142682	-0.890157	1.467407
H	1.222275	0.871944	1.338696
Ir	4.984410	0.637099	-3.710226

12. $Ir_3(PET)_1$ – isomer (l)

C	13.270123	13.274979	15.949681
C	12.232931	12.426127	15.539853
C	10.942210	12.960675	15.413535
C	10.695651	14.306325	15.687708
C	11.738190	15.141886	16.095430
C	13.027399	14.622112	16.224917
C	12.487957	10.961235	15.270138
C	12.138899	10.101990	16.489930
S	12.491080	8.313208	16.180427
Ir	11.012711	7.098787	17.343752
Ir	8.948935	7.742941	16.349402
Ir	10.833370	7.492534	14.916942
H	11.074155	10.173908	16.750078
H	12.742944	10.375066	17.366737
H	13.542447	10.808495	14.996320
H	11.877758	10.617537	14.421047
H	10.123744	12.313651	15.091400
H	9.686674	14.705226	15.578533
H	11.547192	16.194146	16.306682
H	13.848631	15.268078	16.537042
H	14.282234	12.876455	16.046388

13. $Ir_2(PET)_1$ – isomer (m)

C	7.751063	12.595023	12.694163	-0.055483
C	8.409786	11.379385	12.890548	-0.086312

C	9.743896	11.364585	13.299167	-0.129226
C	10.442686	12.560153	13.519162	0.188134
C	9.769854	13.773749	13.319005	-0.131006
C	8.434856	13.792916	12.911375	-0.084929
C	11.897592	12.535782	13.925819	-0.085551
C	12.814291	12.482079	12.692916	-0.011530
S	14.582768	12.475473	13.241963	-0.255361
Ir	15.833695	11.890446	11.562621	60.234740
H	10.296673	14.714296	13.493019	0.048737
H	7.926430	14.746750	12.767557	0.058803
H	6.707854	12.609159	12.378311	0.056693
H	7.881156	10.439371	12.729881	0.058228
H	10.249922	10.410046	13.458282	0.047684
H	12.673625	13.368356	12.060671	0.085053
H	12.610939	11.590049	12.089536	0.057265
H	12.096403	11.661337	14.562505	0.059325
H	12.141887	13.428841	14.519245	0.055477
Ir	16.925448	13.207583	10.165456	59.889378

14. $Ir_2(PET)_1$ – isomer (n)

C	4.095057	7.425062	7.907180	-0.054201
C	4.788723	6.246216	8.188135	-0.085977
C	6.160861	6.284315	8.441474	-0.127900
C	6.863005	7.497440	8.419626	0.191214
C	6.154370	8.674361	8.137721	-0.132774

C	4.782489	8.640607	7.884235	-0.087892
C	8.355139	7.534097	8.656212	-0.066716
C	9.132641	7.438382	7.338615	0.023217
S	10.968433	7.351162	7.664797	-0.178672
Ir	12.067099	8.205618	6.010277	59.996803
H	6.685203	9.628507	8.122627	0.051138
H	4.247932	9.567044	7.672096	0.058099
H	3.022950	7.397488	7.711900	0.056626
H	4.258739	5.293598	8.214947	0.057891
H	6.695715	5.359296	8.666824	0.046949
H	8.937107	8.289743	6.679350	0.085884
H	8.898582	6.507310	6.801492	0.058669
H	8.649613	6.707093	9.320228	0.058529
H	8.638681	8.470181	9.160214	0.035474
Ir	11.748529	9.327967	8.077383	60.013599