SUPPORTING INFORMATION

Cyclometalated Iridium(III) Complexes of Azadipyrromethene Chromophores

Nihal Deligonul,[†] Amberle R. Browne,[†] James A. Golen,[‡] Arnold L. Rheingold,[‡] and Thomas G. Gray[†,*]

Department of Chemistry, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106, and Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093

Contents

Synthesis of [Ir(tpy)$_2$(L$_a$)] (8). Under Ar(g), potassium hydroxide (22 mg, 0.39 mmol) dissolved in de-ionized H_2O (1 mL) was added to a solution of $BF_2 \cdot \mathbf{L_a}$ (50 mg, 0.10 mmol) in THF (10 mL) giving a teal solution. After stirring the mixture for 30 min, *cis*-[Ir(tpy)$_2$(H$_2$O)$_2$]OTf (85 mg, 0.12 mmol) dissolved in THF (1 mL) was added dropwise, and the reaction mixture was allowed to stir at room temperature for 24 h resulting in a deep blue mixture. The solvent was removed by rotary evaporation to give a violet residue. Compound **8** was separated from the residue by preparatory thin layer chromatography (CH_2Cl_2/hexanes, 1:1, v/v) and further purified by the vapor diffusion of pentane into a concentrated CH_2Cl_2 solution to give purple crystals with a red luster. Yield: 39 mg (40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, 2H, J = 5.7 Hz), 7.82 (dd, 4H, J = 7.6, 1.8 Hz), 7.61 (m, 2H), 7.45 (d, 2H, J = 8.1 Hz), 7.32 – 7.28 (m, 6H), 7.01 (t, 2H, J = 6.9 Hz), 6.91 (t, 2H, J = 7.4 Hz), 6.86 (d, 2H, J = 7.9 Hz), 6.71 (t, 4H, J = 7.6 Hz), 6.61 (s, 2H), 6.57 (d, 4H, J = 7.8 Hz), 6.18 (d, 2H, J = 8.0 Hz), 5.39 (s, 2H), 1.70 (s, 6H). Anal. Calc. for $C_{56}H_{42}IrN_5$ (%): C, 68.83; H, 4.33; N, 7.17. Found: C, 70.22; H, 4.47; N, 7.36.

Absorption (blue) and emission (red) of [Ir(tpy)$_2$(L$_a$)] (8) in $CHCl_3$

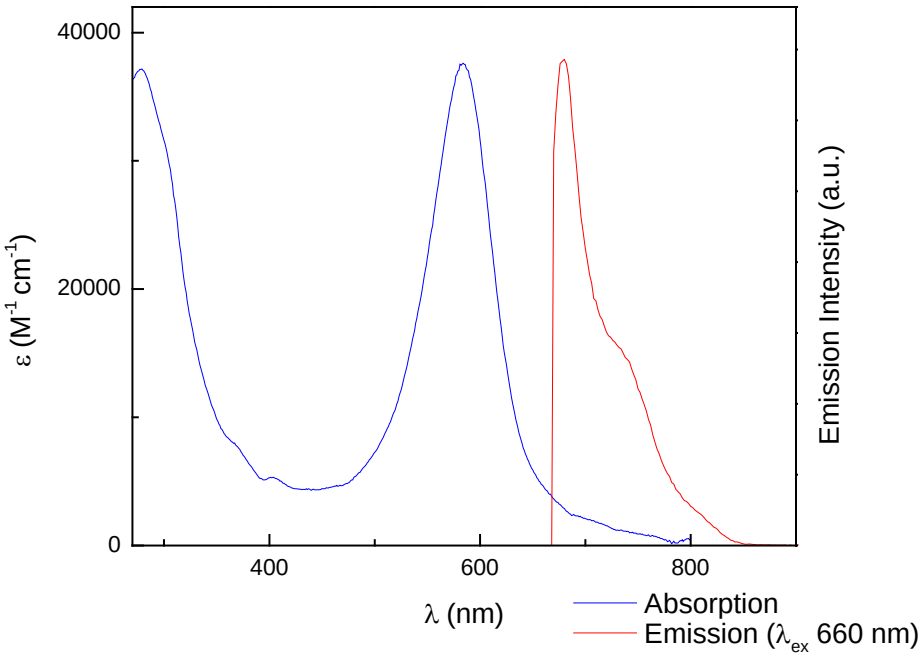

Table S1. Crystallographic data.

Experiments were carried out at 100 K with Mo *K*α radiation. Absorption was corrected for by multi-scan methods, *SADABS*. Refinement was with 0 restraints. H-atom parameters were constrained.

	$[Ir(ppy)_2(\mathbf{L_aBr_2})]$	$[Ir(bt)_2(\mathbf{L_aBr_2})]$
Crystal data		
Chemical formula	$C_{58}H_{44}Br_2IrN_5O$	$C_{58}H_{36}Br_2IrN_5S_2$
M_r	1179.00	1219.06
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$
a, *b*, *c* (Å)	8.6976 (8), 14.2957 (14), 19.3546 (19)	9.4840 (5), 40.549 (2), 12.0231 (6)
α, β, γ (°)	95.158 (4), 95.079 (4), 107.554 (4)	90, 94.717 (2), 90
V (Å^3)	2268.2 (4)	4608.0 (4)
Z	2	4
μ (mm^{-1})	4.76	4.77
Crystal size (mm^3)	0.30 × 0.10 × 0.05	0.14 × 0.08 × 0.04
Data collection		
Diffractometer	CCD area detector diffractometer	Bruker CMOS area detector diffractometer
T_{min}, T_{max}	0.330, 0.797	0.555, 0.832
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19444, 8911, 7278	32147, 8755, 7230
R_{int}	0.040	0.037
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625	0.611
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.056, 0.120, 1.03	0.032, 0.057, 1.04
No. of reflections	8911	8755
No. of parameters	605	613
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.50, -1.80	1.01, -0.71

Computer programs: Bruker *SMART*, Bruker *APEX2*, Bruker *SAINT*, *SHELXS97* (Sheldrick, 1990), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 1997), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

Figure S1. Emission spectra of new complexes in chloroform solution under ultraviolet excitation (see experimental section).

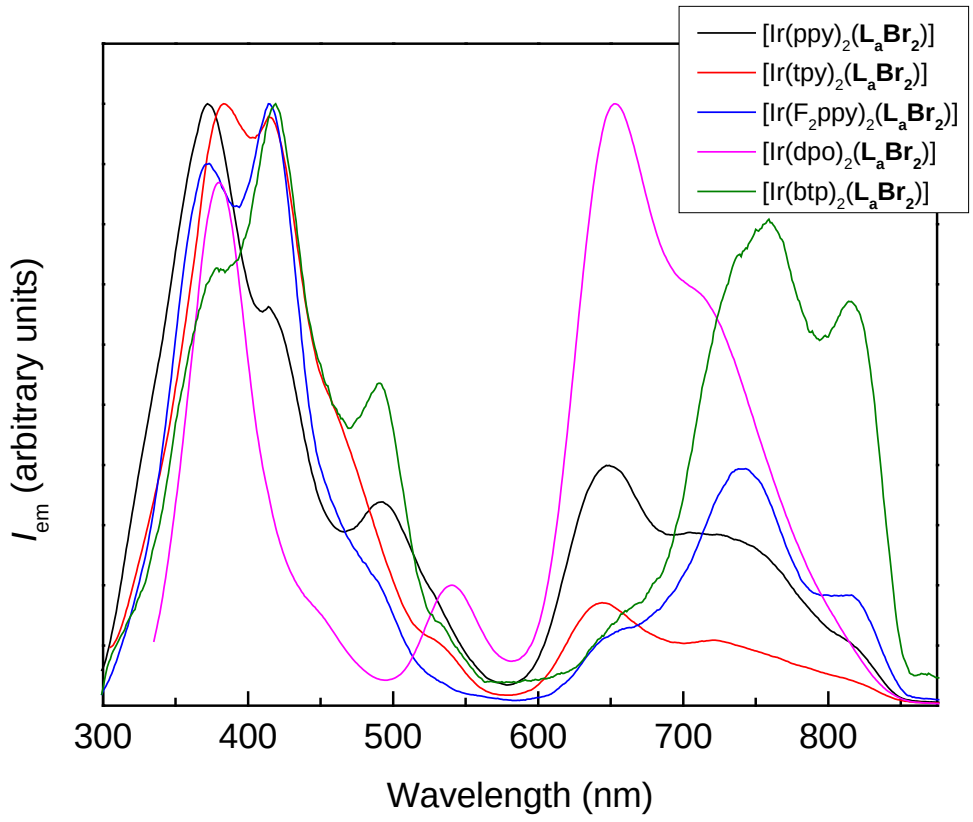

Table S2. Photophysical properties of iridium(III) complexes

Complex	Abs. λ_{max} [nm] ($\varepsilon \times 10^{-3}$)[a]	λ_{exc}[nm][b]	λ_{em} [nm][c]
Ir(ppy)$_2$(**L$_a$Br$_2$**)	265 (47.3), 363$_{sh}$ (7.2), 403$_{sh}$(4.8), 579(40.9)	265	375, 418$_{sh}$, 494$_{sh}$, 652, 729$_{sh}$, 815$_{sh}$
Ir(tpy)$_2$(**L$_a$Br$_2$**)	273 (48.5), 365$_{sh}$ (9.3), 400$_{sh}$ (5.7), 579 (45.2)	274	384, 418$_{sh}$, 532$_{sh}$, 674, 729$_{sh}$
Ir(bzq)$_2$(**L$_a$Br$_2$**)	353 (14.6)$_{sh}$, 393 (8.3)$_{sh}$, 579 (44.2)	326	382$_{sh}$, 406, 654, 734$_{sh}$
Ir(bt)$_2$(**L$_a$Br$_2$**)	321 (27.3), 586 (40.3)	250	376$_{sh}$, 419, 489$_{sh}$, 761, 816$_{sh}$
Ir(F$_2$ppy)$_2$(**L$_a$Br$_2$**)	254 (51.7), 381$_{sh}$ (5.2), 538 (46.1)	253	364$_{sh}$, 413, 645$_{sh}$, 736, 816$_{sh}$
Ir(pq)$_2$(**L$_a$Br$_2$**)	281 (25.0), 355 (9.0), 596 (21.9)	280	348, 355, 596, 655, 731$_{sh}$
Ir(dpo)$_2$(**L$_a$Br$_2$**)	294 (36.2), 406 (5.9), 427 (6.4), 584 (28.7)	298	377, 537, 656$_{sh}$, 712 $_{sh}$

Table S3. Electrochemical properties of iridium(III) complexes.

	E_{red}(V)	E_{red}(V)	$E_{1/2}$(red)(V)	$E_{1/2}$(ox)(V)
$BF_2 \cdot \mathbf{L_aBr_2}$	-	-	-1.51,- 0.70	-
$Ir(ppy)_2(\mathbf{L_aBr_2})$	-2.11	-0.96	-1.45	0.96
$Ir(tpy)_2(\mathbf{L_aBr_2})$	-2.11	-0.99	-148	0.47
$Ir(bzq)_2(\mathbf{L_aBr_2})$	-2.04	-0.96	-1.46	0.48
$Ir(F_2ppy)_2(\mathbf{L_aBr_2})$	-2.03	-0.89	-1.37	0.61
$Ir(bt)_2(\mathbf{L_aBr_2})$	-2.14	-0.99	-1.46	0.50
$Ir(pq)_2(\mathbf{L_aBr_2})$	-2.16	-0.99	-1.51	0.47
$Ir(dpo)_2(\mathbf{L_aBr_2})$	-2.10	-0.85, -0.40	-1.40	0.57

Figure S2. π-Stacking interactions in $[Ir(ppy)_2(\mathbf{L_aBr_2})]$. Distances between benzene-ring centroids (yellow spheres) stated in Å.

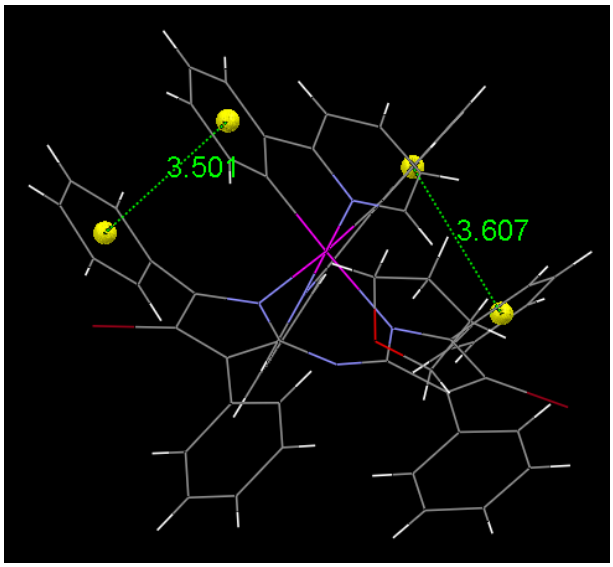

Figure S3. Intramolecular π-Stacking interactions in $[Ir(bt)_2(\mathbf{L_aBr_2})]$. Distances between benzene-ring centroids (yellow spheres) stated in Å.

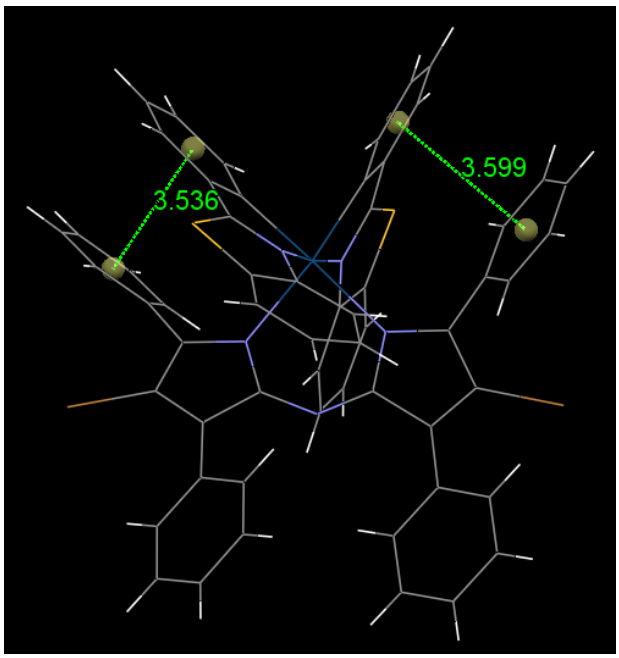

Figure S4. Partial Kohn-Sham orbital energy diagram of [Ir(bt)$_2$(**L$_a$Br$_2$**)] with continuum (IEFPCM) chloroform solvation. Frontier orbital images appear at right (contour level 0.03 a.u.).

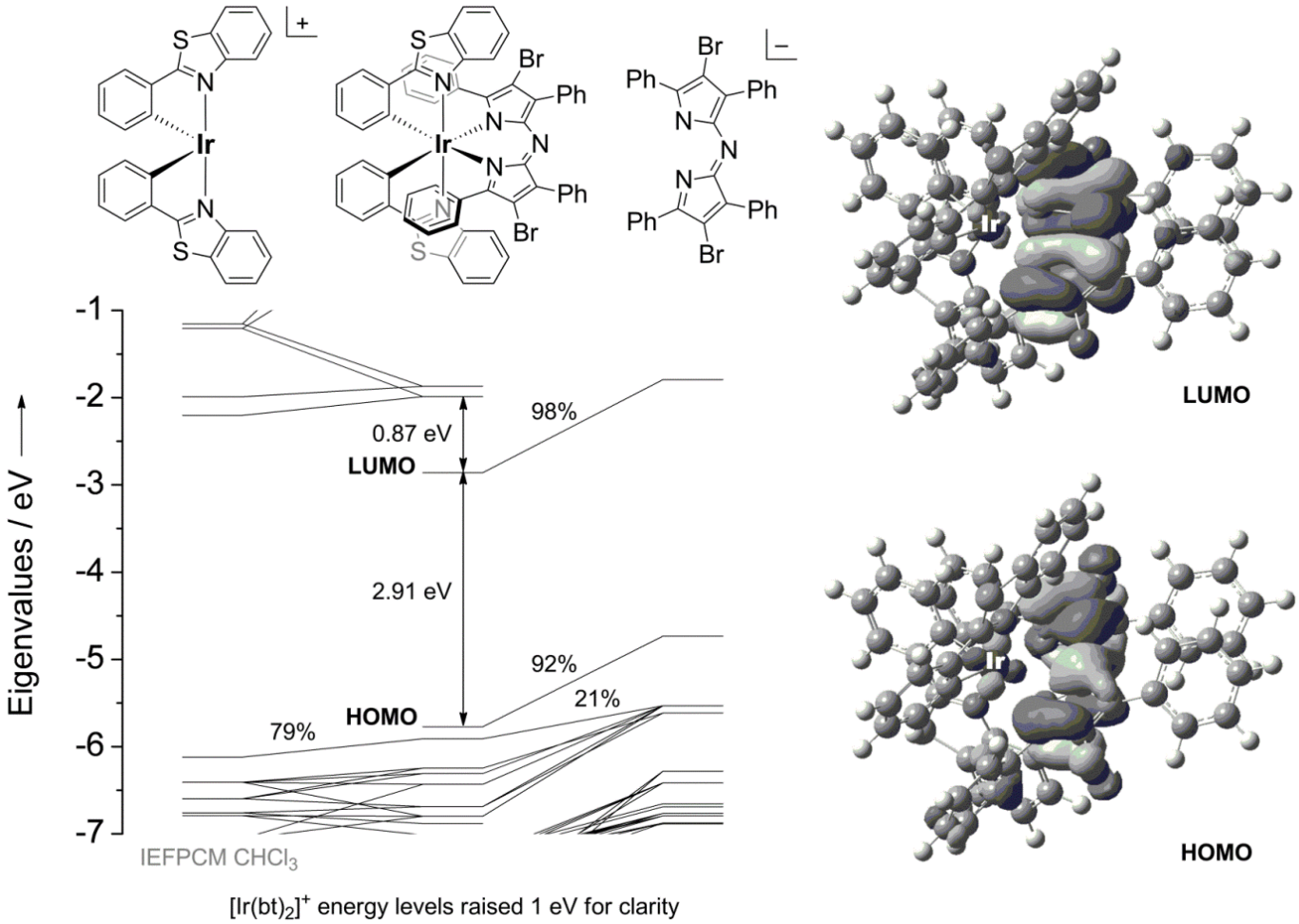

Table S5. Optimized Cartesian coordinates of [Ir(ppy)$_2$**L$_a$Br$_2$**].

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-1.776299	8.603082	5.369221
2	7	0	-3.384313	7.413390	4.822997
3	6	0	-3.606066	6.169870	5.266313
4	1	0	-2.886615	5.782373	5.973409
5	6	0	-4.685024	5.412981	4.860217
6	1	0	-4.813696	4.412050	5.251073
7	6	0	-5.577280	5.966131	3.950936
8	1	0	-6.431614	5.399562	3.598881
9	6	0	-5.367225	7.256130	3.509381
10	1	0	-6.058219	7.713608	2.813936
11	6	0	-4.268007	7.984140	3.964917
12	6	0	-3.983112	9.372189	3.638694

13	6	0	-4.832613	10.163189	2.859221
14	1	0	-5.727902	9.741782	2.414421
15	6	0	-4.547646	11.501497	2.666986
16	1	0	-5.208320	12.120285	2.070109
17	6	0	-3.408531	12.046821	3.254337
18	1	0	-3.180927	13.098517	3.111014
19	6	0	-2.559931	11.259259	4.016637
20	1	0	-1.677500	11.714598	4.452049
21	6	0	-2.815943	9.902567	4.225692
22	7	0	-0.347684	9.940396	5.973795
23	6	0	0.923110	9.928298	5.557951
24	1	0	1.182384	9.125054	4.881383
25	6	0	1.844966	10.870983	5.962624
26	1	0	2.861778	10.821382	5.595016
27	6	0	1.429146	11.870349	6.834716
28	1	0	2.119526	12.639444	7.161564
29	6	0	0.130584	11.857139	7.301650
30	1	0	-0.203354	12.603643	8.010055
31	6	0	-0.754568	10.865074	6.881623
32	6	0	-2.105822	10.659676	7.378853
33	6	0	-2.712957	11.482267	8.328976
34	1	0	-2.198923	12.357731	8.711900
35	6	0	-3.981783	11.185048	8.792795
36	1	0	-4.458236	11.824653	9.527244
37	6	0	-4.637739	10.056860	8.308409
38	1	0	-5.633238	9.817370	8.670049
39	6	0	-4.036738	9.239671	7.360666
40	1	0	-4.582554	8.376017	6.995734
41	6	0	-2.760374	9.517078	6.867915
42	7	0	-0.717687	7.702325	3.622714
43	7	0	-0.404652	5.529927	4.658678
44	7	0	-0.769280	7.020146	6.542692
45	6	0	-0.593873	8.095842	2.355350
46	6	0	-0.341473	6.968404	1.509191
47	6	0	-0.307075	5.837870	2.283537
48	6	0	-0.523244	6.321078	3.625237
49	6	0	-0.453510	5.803371	5.939355
50	6	0	-0.170910	4.804734	6.937122
51	6	0	-0.312500	5.471493	8.130711
52	6	0	-0.658213	6.828113	7.857678
53	6	0	-0.088528	4.443815	1.903688
54	6	0	-0.923117	3.440621	2.405043
55	1	0	-1.725758	3.708228	3.081002
56	6	0	-0.735285	2.116984	2.039070
57	1	0	-1.395266	1.352282	2.433726
58	6	0	0.293148	1.769473	1.172793
59	1	0	0.440362	0.733348	0.888374
60	6	0	1.134290	2.756595	0.674842
61	1	0	1.944953	2.493336	0.004158
62	6	0	0.944066	4.082459	1.033755
63	1	0	1.609455	4.845202	0.647284
64	6	0	-0.636136	9.478387	1.852068
65	6	0	-1.609843	9.857887	0.928576
66	1	0	-2.391893	9.158133	0.658417
67	6	0	-1.592458	11.125113	0.369429
68	1	0	-2.364296	11.410526	-0.336540

69	6	0	-0.592022	12.026084	0.710400
70	1	0	-0.575798	13.015790	0.267218
71	6	0	0.390202	11.651686	1.616409
72	1	0	1.183063	12.343987	1.878054
73	6	0	0.370752	10.384135	2.180041
74	1	0	1.159509	10.086951	2.858745
75	6	0	0.209041	3.414434	6.692307
76	6	0	-0.385136	2.379805	7.421691
77	1	0	-1.141790	2.614275	8.161164
78	6	0	-0.028495	1.059058	7.197487
79	6	0	0.931995	0.746772	6.243684
80	1	0	1.212963	-0.286191	6.070055
81	6	0	1.528603	1.765949	5.512769
82	1	0	-0.505068	0.269988	7.769009
83	1	0	2.278638	1.531953	4.765234
84	6	0	1.170501	3.087456	5.731962
85	1	0	1.637289	3.877911	5.158484
86	6	0	-0.751026	7.854545	8.910102
87	6	0	0.311055	8.734896	9.104873
88	1	0	1.151307	8.718403	8.419489
89	6	0	0.308033	9.610741	10.181461
90	1	0	1.143097	10.287665	10.325084
91	6	0	-0.755982	9.616518	11.071638
92	1	0	-0.758026	10.299958	11.913768
93	6	0	-1.818130	8.741123	10.882724
94	1	0	-2.654469	8.743465	11.572852
95	6	0	-1.810634	7.857529	9.815553
96	1	0	-2.633925	7.166061	9.677313
97	35	0	-0.104428	7.073389	-0.352557
98	35	0	0.045288	4.810390	9.853701

Table S6. Optimized Cartesian coordinates of [Ir(bt)$_2$**L$_a$Br$_2$**].

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.865838	-0.737529	0.408512
2	7	0	0.185172	-0.650703	2.215830
3	6	0	0.677975	0.374408	3.012262
4	6	0	0.477138	1.745115	2.854680
5	6	0	1.047190	2.614710	3.766337
6	6	0	1.801219	2.146686	4.844092
7	6	0	1.979233	0.788218	5.039645
8	6	0	1.400063	-0.082602	4.127781
9	6	0	0.442692	-1.841102	2.720545
10	6	0	-0.137961	-2.998277	2.105470
11	6	0	-0.883361	-2.695533	0.946107
12	6	0	-1.576843	-3.758539	0.365257
13	6	0	-1.519173	-5.037293	0.899250
14	6	0	-0.763071	-5.310582	2.038941
15	6	0	-0.066323	-4.285951	2.645249
16	1	0	-0.118859	2.116595	2.035250

17	1	0	0.897820	3.680939	3.641735
18	1	0	2.240952	2.849739	5.541786
19	1	0	2.541314	0.414437	5.887158
20	1	0	-2.168951	-3.595205	-0.527787
21	1	0	-2.070409	-5.840136	0.420011
22	1	0	-0.726499	-6.314714	2.445371
23	1	0	0.515875	-4.476715	3.542106
24	16	0	1.394314	-1.827001	4.173096
25	7	0	-2.109426	-0.961492	-1.221226
26	6	0	-3.365855	-1.207155	-0.901119
27	6	0	-3.740602	-1.139690	0.480952
28	6	0	-5.029927	-1.366303	0.966154
29	6	0	-5.280500	-1.217289	2.315987
30	6	0	-4.241173	-0.834949	3.163700
31	6	0	-2.960903	-0.610523	2.676815
32	6	0	-2.666078	-0.757389	1.319610
33	6	0	-1.920200	-0.854438	-2.587175
34	6	0	-0.750661	-0.474377	-3.243061
35	6	0	-0.755382	-0.407538	-4.624097
36	6	0	-1.903742	-0.712032	-5.359839
37	6	0	-3.078014	-1.073648	-4.721539
38	6	0	-3.077506	-1.123500	-3.334226
39	1	0	-5.829739	-1.656289	0.291022
40	1	0	-6.273990	-1.393689	2.711644
41	1	0	-4.436226	-0.714956	4.225033
42	1	0	-2.179475	-0.324038	3.372168
43	1	0	0.134565	-0.243457	-2.665521
44	1	0	0.148177	-0.110599	-5.143782
45	1	0	-1.880449	-0.656499	-6.441849
46	1	0	-3.975405	-1.292844	-5.287621
47	16	0	-4.415610	-1.462595	-2.262889
48	7	0	1.151575	-0.948543	-0.517376
49	7	0	1.719393	1.398652	-0.364196
50	7	0	-0.700085	1.382725	-0.141888
51	6	0	1.904625	-2.020797	-0.770697
52	6	0	3.291478	-1.654799	-0.780864
53	6	0	3.392180	-0.306747	-0.552411
54	6	0	2.025907	0.130111	-0.407677
55	6	0	0.545468	1.978355	-0.337377
56	6	0	0.405067	3.401924	-0.490328
57	6	0	-0.950289	3.616523	-0.405016
58	6	0	-1.599493	2.365675	-0.195845
59	6	0	1.422545	-3.363630	-1.123488
60	6	0	0.605550	-3.545217	-2.239536
61	6	0	0.249876	-4.819646	-2.653417
62	6	0	0.704158	-5.931568	-1.957591
63	6	0	1.514780	-5.759985	-0.843222
64	6	0	1.880090	-4.487491	-0.434401
65	6	0	4.566611	0.561450	-0.506994
66	6	0	5.569464	0.464692	-1.476199
67	6	0	6.676036	1.298605	-1.434604
68	6	0	6.803339	2.240969	-0.421897
69	6	0	5.812053	2.348056	0.544972
70	6	0	4.701753	1.518723	0.503150
71	6	0	1.489030	4.358390	-0.705025
72	6	0	2.519454	4.090922	-1.611227

73	6	0	3.544789	5.004185	-1.803788
74	6	0	3.562503	6.199015	-1.096153
75	6	0	2.545640	6.474645	-0.190624
76	6	0	1.517875	5.564718	0.001803
77	6	0	-3.065605	2.242347	-0.090144
78	6	0	-3.707235	2.417958	1.133506
79	6	0	-5.091764	2.432446	1.202242
80	6	0	-5.849227	2.284975	0.047573
81	6	0	-5.216303	2.117742	-1.175857
82	6	0	-3.830155	2.099895	-1.245717
83	1	0	-3.334961	1.988410	-2.204522
84	1	0	0.260816	-2.683350	-2.795647
85	1	0	-0.378718	-4.942930	-3.528724
86	1	0	0.428260	-6.928946	-2.282280
87	1	0	1.867304	-6.622722	-0.288939
88	1	0	2.513875	-4.362669	0.435232
89	1	0	5.471681	-0.258297	-2.276996
90	1	0	7.440746	1.214426	-2.199109
91	1	0	7.670380	2.891577	-0.388386
92	1	0	5.902126	3.083224	1.337049
93	1	0	3.930064	1.606228	1.258049
94	1	0	2.511457	3.160953	-2.164799
95	1	0	4.335176	4.779679	-2.511611
96	1	0	4.366020	6.911400	-1.247886
97	1	0	2.554349	7.401673	0.372323
98	1	0	0.735002	5.782407	0.718587
99	1	0	-3.117393	2.544383	2.033997
100	1	0	-5.581003	2.561756	2.161188
101	1	0	-6.932243	2.303161	0.102005
102	1	0	-5.801717	2.005925	-2.081809
103	35	0	4.711138	-2.845467	-1.101100
104	35	0	-1.873043	5.239260	-0.622236