Shedding light on unusual photophysical properties of bis-cyclometalated iridium complexes containing 2,5-diaryl-1,3,4-oxadiazole-based and acetylacetonate ligands

Gahungu Godefroid [a,b], Su Juanjuan [a], Liu Yuqi [a], Qu Xiaochun [a], Yanling Si [a,c] and Wu Zhijian [a]

[a] *State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China.*

[b] *Université du Burundi, Faculté des Sciences, Département de Chimie, Unité de Chimie Théorique et Modélisation Moléculaire, Bujumbura BP. 2700, Burundi.*

[c] *College of Resource and Environmental Science, Jilin Agricultural University, Changchun, Jilin 130118, P.R China.*

Supporting Information

Table S1. Bond lengths (Å), and torsional angles (°) for **2a**, **2b** and **4b** in the S_0 state.*

	2a		**2b**		**4b**	
Parameter	***a***	***b***	***a***	***b***	***a***	***b***
C_1-C_2	1.401	1.401	1.401	1.402	1.401	1.402
C_2-C_3	1.391	1.391	1.391	1.391	1.391	1.391
C_3-C_4	1.397	1.397	1.398	1.395	1.398	1.395
C_4-C_5	1.388	1.388	1.389	1.389	1.389	1.389
C_5-C_6	1.403	1.403	1.402	1.403	1.402	1.402
C_6-C_1	1.431	1.431	1.431	1.431	1.430	1.430
C_6-C_7	1.430	1.430	1.431	1.436	1.433	1.438
C_7-N_8	1.318	1.318	1.319	1.312	1.317	1.311
N_8-N_9	1.373	1.373	1.372	1.375	1.377	1.380
N_9-C_{10}	1.302	1.302	1.302	1.302	1.299	1.298
C_{10}-O_{11}	1.382	1.382	1.382	1.380	1.390	1.388
O_{11}-C_7	1.348	1.348	1.348	1.352	1.345	1.349
C_{10}-C_{12}	1.453	1.453	1.453	1.454	1.473	1.473
C_{12}-C_{13}	1.405	1.405	1.405	1.404	1.413	1.417
C_{13}-C_{14}	1.392	1.392	1.392	1.392	1.398	1.398
C_{14}-C_{15}	1.391	1.391	1.391	1.391	1.397	1.399
C_{15}-C_{16}	1.393	1.393	1.393	1.393	1.399	1.397
C_{16}-C_{17}	1.390	1.390	1.390	1.390	1.397	1.398
C_{17}-C_{12}	1.407	1.407	1.407	1.407	1.416	1.414
C_1-Ir	2.028	2.028	2.022	2.035	2.024	2.034
N_8-Ir	2.052	2.052	2.037	2.197	2.036	2.193
ϕ [a]	0.52	0.52	0.46	0.21	0.30	0.20
ω [b]	0.30	0.30	1.59	0.25	66.49	64.61

*See Figures 1-2 for labeling scheme; [a] $\phi = C_1$-C_6-C_7-N_8; [b] $\omega = O_{11}$-C_{10}-C_{12}-C_{13}

nTable S2. Variations for selected bond lengths and torsional angles (in Å and °, respectively) upon $S_0 \rightarrow T_1$ transition for **2a**, **2b** and **4b**.

	2a		**2b**		**4b**	
	a	***b***	***a***	***b***	***a***	***b***
C_6-C_1	0.018	0.018	0.035	-0.002	0.045	-0.002
C_5-C_6	0.007	0.007	0.027	-0.001	0.035	-0.001
C_6-C_7	-0.017	-0.017	-0.052	0.002	-0.062	0.002
C_7-N_8	0.020	0.020	0.079	-0.002	0.088	-0.002
N_8-N_9	-0.020	-0.020	-0.057	-0.000	-0.039	-0.000
N_9-C_{10}	0.011	0.011	0.037	0.000	0.018	0.001
O_{11}-C_7	0.012	0.012	0.028	-0.001	0.031	-0.002
C_{10}-C_{12}	-0.010	-0.010	-0.031	-0.000	-0.010	-0.001
N_8-Ir	-0.007	-0.007	-0.065	0.020	-0.070	0.026
ϕ [a]	0.31	0.31	-0.13	-0.45	-0.72	-0.40
ω [b]	-1.11	-1.11	-0.72	1.15	15.69	-2.20

*See Figures 1-2 for labeling scheme; [a] $\phi = C_1$-C_6-C_7-N_8; [b] $\omega = O_{11}$-C_{10}-C_{12}-C_{13}

Table S3. Highest occupied and lowest virtual orbitals for N,N-*trans* isomers of Ir(oxd^1)$_2$(*acac*), Ir(oxd^2)$_2$(*acac*) and Ir(oxd^3)$_2$(*acac*).

Orbital	E (eV)	oxd^2_a	*Ir*	*Acac*	Oxd^2_b	Character
Ir(oxd^1)$_2$(*acac*)						
L+3	-0.99	48	3	1	48	π (*oxd*)*
L+2	-1.03	48	4	1	48	π (*oxd*)*
L+1	-1.75	49	1	0	49	π (*oxd*)*
L	-1.80	50	1	0	50	π (*oxd*)*
H	-5.33	25	45	6	25	5d (45%) + π (*oxd*)
H-1	-5.36	5	24	67	5	5d (24%) + π (*acac*)
H-2	-5.91	37	7	19	37	5d (7%) + π (*oxd*)
H-3	-5.96	28	38	7	28	5d (38%) + π (*oxd*)
Ir(*oxd*)$_2$(*acac*)						
L+3	-0.91	47	4	1	47	π (*oxd*)*
L+2	-0.95	48	4	1	48	π (*oxd*)*
L+1	-1.69	50	1	0	50	π (*oxd*)*
L	-1.74	50	1	0	50	π (*oxd*)*
H	-5.25	24	45	6	24	5d (45%) + π (*oxd*)
H-1	-5.29	5	24	67	5	5d (24%) + π (*acac*)
H-2	-5.84	36	8	20	36	5d (8%) + π (*oxd*)
H-3	-5.89	27	39	7	27	5d (39%) + π (*oxd*)
Ir(oxd^3)$_2$(*acac*)						
L+3	-0.62	24	2	1	73	π (*oxd*)*
L+2	-0.65	73	2	1	24	π (*oxd*)*
L+1	-1.23	41	3	1	56	π (*oxd*)*
L	-1.32	56	2	0	41	π (*oxd*)*
H	-5.21	21	46	9	24	5d (46%) + π (*oxd*)
H-1	-5.26	6	26	64	4	5d (26%) + π (*acac*)
H-2	-5.88	49	22	15	13	5d (22%) + π (*oxd*)
H-3	-5.88	8	34	12	47	5d (34%) + π (*oxd*)

Table S4. Highest occupied and lowest virtual orbitals for N,N-*cis* isomers of Ir(*oxd*^{1})$_2$(*acac*), Ir(*oxd*^{2})$_2$(*acac*) and Ir(*oxd*^{3})$_2$(*acac*).

Orbital	E (eV)	*oxd*^{2}$_a$	Ir	*acac*	*oxd*^{2}$_b$	Character
Ir(*oxd*^{1})$_2$(*acac*)						
L+3	-0.86	2	2	9	88	π (*oxd*)*
L+2	-1.00	93	3	1	2	π (*oxd*)*
L+1	-1.65	2	1	0	97	π (*oxd*)*
L	-1.78	97	1	0	2	π (*oxd*)*
H	-5.33	27	44	11	19	5d (44%) + π (*oxd*)
H-1	-5.46	8	35	38	19	5d (35%) + π (*acac*)
H-2	-5.90	30	37	23	10	5d (37%) + π (*oxd+acac*)
H-3	-5.96	20	11	11	58	π (*oxd*)
Ir(*oxd*)$_2$(*acac*)						
L+3	-0.69	2	2	6	89	π (*oxd*)*
L+2	-0.84	92	4	1	3	π (*oxd*)*
L+1	-1.51	2	1	0	97	π (*oxd*)*
L	-1.64	97	1	0	2	π (*oxd*)*
H	-5.06	24	46	10	20	5d (46%) + π (*oxd*)
H-1	-5.22	11	39	33	17	5d (39%) + π (*acac+oxd*)
H-2	-5.60	27	39	24	10	5d (39%) + π (*oxd+acac*)
H-3	-5.86	20	8	16	56	π (*oxd*)
Ir(*oxd*^{3})$_2$(*acac*)						
L+3	-0.65	92	2	6	0	π (*oxd*)*
L+2	-0.68	6	2	91	1	π (*acac*)*
L+1	-1.12	5	2	1	92	π (*oxd*)*
L	-1.28	91	2	1	6	π (*oxd*)*
H	-5.22	23	46	13	17	5d (46%) + π (*oxd*)
H-1	-5.34	8	37	36	18	5d (37%) + π (*acac+oxd*)
H-2	-5.77	29	41	21	9	5d (41%) + π (*oxd+acac*)
H-3	-5.94	19	9	13	58	π (*oxd*)

Table S5. Highest occupied and lowest virtual orbitals for N,N-*cis* Ir(*oxd*^{2})$_2$(*acac*) in the twisted conformation of N,N-*cis* Ir(*oxd*^{3})$_2$(*acac*).

Orbital	MO (eV	*oxd*^{2}$_a$	Ir	*Acac*	*Oxd*^{2}$_b$	Character
L+3	-0.77	51	2	9	38	π (*oxd*)*
L+2	-0.91	15	3	55	27	π (*acac*)*
L+1	-1.20	33	1	6	60	π (*oxd*)*
L	-1.35	30	2	17	51	π (*oxd*)*
H	-5.23	22	46	0	31	5d (46%) + π (*oxd*)
H-1	-5.35	24	38	0	38	5d (38%) + π (*oxd*)
H-2	-5.78	38	41	0	20	5d (41%) + π (*oxd*)
H-3	-5.98	27	10	1	63	π (*oxd*)

Table S6: Calculated excited energies, dominant orbital excitations, and oscillator strength (*f*) from PCM-TD-CAM-B3LYP calculations for the N,N-*trans* series.

	St	E_{th}	λ_{cal}	*f*	Excitation (contribution)	Character
1a	S_1	3.56	348.1	0.340	H->L (66%), H->L+2 (20%)	MLCT/LLCT/LC
	S_2	3.68	336.6	0.020	H->L+1 (60%), H->L+3 (20%)	MLCT/LLCT/LC
	S_3	4.14	299.3	0.069	H-1->L (58%), H-1->L+2 (12%)	MLCT/LLCT
	S_4	4.14	299.2	0.163	H-1->L+1 (53%), H-1->L+3 (16%)	MLCT/LLCT
	S_5	4.40	281.9	0.408	H-3->L (58%)	MLCT/LLCT/LC
	S_6	4.45	278.9	0.137	H-3->L+1 (51%), H-2->L (15%)	MLCT//LC
	S_7	4.53	273.7	0.362	H-1->L+4 (51%)	MLCT/LLCT/LC
	S_8	4.59	270.0	0.411	H-1->L+4 (35%), H->L+2 (14%)	MLCT/LLCT/LC
	S_9	4.63	268.0	0.016	H-5->L+1 (11%), H-2->L (14%)	MLCT/LLCT/LC
	S_{10}	4.64	266.9	0.005	H->L+4 (79%)	LLCT/LC
	T_1	2.69	460.1	0.000	H-3->L (17%), H-2->L+1 (23%), H->L (21%)	MLCT/LLCT/LC
	T_2	2.70	459.4	0.000	H-3->L+1 (16%), H-2->L (25%), H-1->L (10%), H->L+1 (18%)	MLCT/LLCT/LC
	T_3	3.00	412.9	0.000	H-2->L+4 (21%), H-1->L+4 (72%)	MLCT/LLCT
2a	S_1	3.68	336.2	0.427	H->L (63%), H->L+2 (17%)	MLCT/LLCT/LC
	S_2	3.79	327.1	0.047	H->L+1 (58%), H->L+3 (16%)	MLCT/LLCT/LC
	S_3	4.21	294.4	0.174	H-1->L+1 (51%), H-1->L+3 (13%)	MLCT/LLCT
	S_4	4.23	293.3	0.064	H-1->L (55%), H-1->L+2 (10%)	MLCT/LLCT
	S_5	4.46	277.8	0.640	H-3->L (47%), H-2->L+1 (16%)	MLCT/LLCT/LC
	S_6	4.50	275.2	0.139	H-3->L+1 (43%), H-2->L (22%)	MLCT//LC
	S_7	4.55	272.3	0.172	H-2->L+4 (11%), H-1->L+4 (67%)	MLCT/LLCT/LC
	S_8	4.63	267.5	0.379	H-1->L+4 (15%), H->L+2 (10%)	MLCT/LLCT/LC
	S_9	4.68	265.0	0.005	H-5->L+1 (11%), H->L+10 (10%)	MLCT/LLCT/LC
	S_{10}	4.75	261.2	0.007	H->L+4 (75%)	LLCT/LC
	T_1	2.72	455.1	0.000	H-3->L (16%), H-2->L+1 (22%), H-1->L+1 (11%), H->L (23%)	MLCT/LLCT/LC
	T_2	2.73	454.8	0.000	H-3->L+1 (15%), H-2->L (24%), H-1->L (13%), H->L+1 (20%)	MLCT/LLCT/LC
	T_3	3.00	412.8	0.000	H-2->L+4 (28%), H-1->L+4 (67%)	MLCT/LLCT
3a	S_1	3.69	335.9	0.419	H->L (63%), H->L+2 (18%)	MLCT/LLCT/LC
	S_2	3.79	326.7	0.046	H->L+1 (57%), H->L+3 (17%)	MLCT/LLCT/LC
	S_3	4.21	294.2	0.168	H-1->L+1 (51%), H-1->L+3 (14%)	MLCT/LLCT
	S_4	4.23	293.1	0.062	H-1->L (54%), H-1->L+2 (11%)	MLCT/LLCT
	S_5	4.47	277.4	0.617	H-3->L (47%), H-2->L+1 (15%)	MLCT/LLCT/LC
	S_6	4.51	274.8	0.140	H-3->L+1 (43%), H-2->L (21%)	MLCT/LLCT/LC
	S_7	4.55	272.3	0.167	H-2->L+4 (10%), H-1->L+4 (69%)	LLCT/LC
	S_8	4.64	267.4	0.368	H-1->L+4 (15%), H->L+2 (11%)	MLCT/LLCT/LC
	S_9	4.68	264.9	0.005	H-5->L+1 (10%), H->L+10 (10%)	MLCT/LLCT/LC
	S_{10}	4.75	261.2	0.007	H->L+4 (76%)	LLCT/LC
	T_1	2.72	455.1	0.000	H-3->L (16%), H-2->L+1 (22%), H-1->L+1 (11%), H->L (22%)	MLCT/LLCT/LC
	T_2	2.73	454.8	0.000	H-3->L+1 (15%), H-2->L (24%), H-1->L (12%), H->L+1 (19%)	MLCT/LLCT/LC
	T_3	3.00	412.7	0.000	H-2->L+4 (26%), H-1->L+4 (68%)	MLCT/LLCT
4a	S_1	3.78	387.8	0.114	H->L (95%)	MLCT/LLCT/LC
	S_2	3.90	374.7	0.005	H->L+1 (89%)	MLCT/LLCT/LC
	S_3	4.29	364.1	0.009	H-1->L (88%)	MLCT/LLCT
	S_4	4.31	359.0	0.018	H-1->L+1 (94%)	MLCT/LLCT
	S_5	4.55	319.0	0.004	H->L+2 (92%)	MLCT/LLCT/LC

	S_6	4.61	317.3	0.054	H-3->L (62%), H-2->L (25%)	MLCT/LLCT/LC
	S_7	4.68	310.8	0.023	H-3->L+1 (56%), H-2->L+1 (25%)	MLCT/LLCT/LC
	S_8	4.75	305.8	0.074	H-3->L (24%), H-2->L (62%)	MLCT/LLCT/LC
	S_9	4.75	301.8	0.152	H-3->L+1 (23%), H-2->L+1 (52%), H-1->L+2 (15%)	MLCT/LLCT/LC
	S_{10}	4.79	298.3	0.038	H-1->L+2 (71%)	MLCT/ LLCT
	T_1	2.89	428.5	0.000	H-3->L (14%), H-2->L+1 (25%), H->L (27%)	MLCT/LLCT/LC
	T_2	2.90	427.8	0.000	H-3->L+1 (14%), H-2->L (28%), H->L+1 (24%)	MLCT/LLCT/LC
	T_3	3.01	412.3	0.000	H-2->L+2 (12%), H-1->L+2 (66%)	MLCT/ LLCT

Table S7. Calculated excited energies, dominant orbital excitations, and oscillator strength (*f*) from PCM-TD-CAM-B3LYP calculations for the N,N-*cis* series.

	St	E_{th}	λ_{cal}	*f*	Excitation (contribution)	Character
1b	S_1	342.6	3.62	0.196	H->L (62%), H->L+2 (18%)	MLCT/LLCT/LC
	S_2	323.2	3.84	0.322	H-1->L+1 (14%), H->L+1 (45%), H->L+3 (12%)	MLCT/LLCT/LC
	S_3	302.8	4.09	0.028	H-1->L (47%), H-1->L+2 (16%)	MLCT/LLCT
	S_4	291.6	4.25	0.101	H-1->L+1 (46%), H-1->L+3 (11%), H->L+1 (16%)	MLCT/LLCT
	S_5	284.3	4.36	0.041	H-2->L (10%), H-1->L+4 (17%), H->L+4 (23%)	LLCT/LC
	S_6	283.3	4.38	0.030	H-2->L (38%), H-2->L+2 (14%)	MLCT//LC
	S_7	281.6	4.40	0.244	H-1->L+4 (16%), H->L+10 (10%)	MLCT/LLCT/LC
	S_8	273.9	4.52	0.067	H-1->L+4 (25%), H->L+4 (33%)	MLCT/LLCT/LC
	S_9	272.4	4.55	0.255	H-3->L+1 (32%), H-2->L+1 (22%)	LLCT/LC
	S_{10}	269.3	4.60	0.320	H-4->L (13%), H-3->L (12%), H->L+2 (17%)	MLCT/LLCT/LC
	T_1	465.0	2.67	0.000	H-4->L (14%), H-3->L (13%), H->L (38%)	MLCT/LLCT/LC
	T_2	450.3	2.75	0.000	H-3->L+1 (32%), H-1->L+1 (17%), H->L+1 (11%)	MLCT/LLCT/LC
	T_3	416.1	2.98	0.000	H-2->L+4 (26%), H-1->L+4 (36%)	MLCT/LLCT/LC
2b	S_1	333.2	3.72	0.257	H->L (62%), H->L+2 (15%)	MLCT/LLCT/LC
	S_2	315.8	3.93	0.386	H-1->L+1 (16%), H->L+1 (45%)	MLCT/LLCT/LC
	S_3	295.1	4.20	0.029	H-1->L (38%), H-1->L+2 (14%)	MLCT/LLCT
	S_4	285.1	4.35	0.163	H-1->L+1 (40%), H->L+1 (15%)	MLCT/LLCT
	S_5	281.8	4.40	0.092	H-1->L+3 (12%), H-1->L+4 (12%)	LLCT/LC
	S_6	279.7	4.43	0.164	H-1->L+4 (27%)	MLCT//LC
	S_7	275.4	4.50	0.034	H-3->L (50%), H-3->L+2 (17%)	MLCT/LLCT/LC
	S_8	270.0	4.59	0.057	H-1->L+3 (11%), H->L+3 (20%), H->L+4 (28%)	MLCT/LLCT/LC
	S_9	268.1	4.62	0.308	H-3->L+1 (12%), H-2->L (13%), H-2->L+1 (11%)	LLCT/LC
	S_{10}	266.5	4.65	0.312	H-4->L (10%), H-3->L+1 (21%)	MLCT/LLCT/LC
	T_1	459.5	2.70	0.000	H-4->L (11%), H-2->L (17%), H->L (41%)	MLCT/LLCT/LC
	T_2	447.2	2.77	0.000	H-2->L+1 (25%), H-1->L+1 (22%), H->L+1 (12%)	MLCT/LLCT/LC
	T_3	415.8	2.98	0.000	H-2->L+4 (17%), H-1->L+3 (18%), H-1->L+4 (29%)	MLCT/LLCT/LC
3b	S_1	333.0	3.72	0.252	H->L (62%), H->L+2 (16%)	MLCT/LLCT/LC
	S_2	315.4	3.93	0.378	H-1->L+1 (16%), H->L+1 (44%)	MLCT/LLCT/LC
	S_3	294.9	4.20	0.030	H-1->L (38%), H-1->L+2 (15%)	MLCT/LLCT
	S_4	284.8	4.35	0.163	H-1->L+1 (38%), H->L+1 (15%)	MLCT/LLCT/LC
	S_5	282.1	4.39	0.078	H-1->L+3 (13%), H-1->L+4 (11%), H->L+3 (10%)	MLCT/LLCT/LC
	S_6	279.6	4.43	0.170	H-1->L+4 (26%)	MLCT/LLCT/LC
	S_7	275.4	4.50	0.034	H-3->L (49%), H-3->L+2 (18%)	MLCT/LLCT/LC
	S_8	269.9	4.59	0.056	H-1->L+3 (11%), H->L+3 (19%), H->L+4 (29%)	MLCT/LLCT
	S_9	267.6	4.63	0.294	H-3->L+1 (15%), H-2->L (11%), H-2->L+1 (10%)	LLCT/LC
	S_{10}	266.0	4.66	0.273	H-3->L+1 (24%)	MLCT/LLCT
	T_1	459.5	2.70	0.000	H-4->L (12%), H-2->L (17%), H->L (40%)	MLCT/LLCT/LC
	T_2	447.5	2.77	0.000	H-2->L+1 (23%), H-1->L+1 (21%), H->L+1 (12%)	MLCT/LLCT/LC
	T_3	415.8	2.98	0.000	H-2->L+4 (17%), H-1->L+3(18%), H-1->L+4 (29%)	MLCT/LLCT/LC
4b	S_1	323.9	3.83	0.120	H->L (74%)	MLCT/LLCT/LC
	S_2	305.4	4.06	0.198	H-1->L (11%), H-1->L+1 (15%), H->L+1 (52%)	MLCT/LLCT/LC
	S_3	291.5	4.25	0.041	H-1->L (39%), H-1->L+1 (14%)	MLCT/LLCT
	S_4	281.1	4.41	0.047	H-1->L+2 (46%), H->L+2 (37%)	MLCT/LLCT/LC
	S_5	278.7	4.45	0.065	H-1->L (15%), H-1->L+1 (35%), H->L+1 (17%)	MLCT/LLCT

	S_6	276.8	4.48	0.041	H-1->L+1 (13%), H->L+12 (11%)	MLCT/LLCT
	S_7	271.8	4.56	0.053	H-3->L (22%), H-2->L (35%)	MLCT/LLCT/LC
	S_8	269.1	4.61	0.009	H-1->L+2 (32%), H->L+2 (42%)	MLCT/LLCT
	S_9	264.2	4.69	0.002	H-1->L+12 (19%)	MLCT/LLCT/LC
	S_{10}	257.4	4.82	0.110	H-3->L+1 (48%), H-2->L+1 (18%)	LLCT/ LC
	T_1	432.8	2.86	0.000	H-2->L (10%), H->L (42%)	MLCT/ LC
	T_2	418.9	2.96	0.000	H-3->L+1 (26%), H-1->L+1 (20%), H->L+1 (12%)	MLCT/LLCT/LC
	T_3	415.9	2.98	0.000	H-2->L+2 (25%), H-1->L+2 (49%), H->L+2 (12%)	MLCT/ LLCT/LC

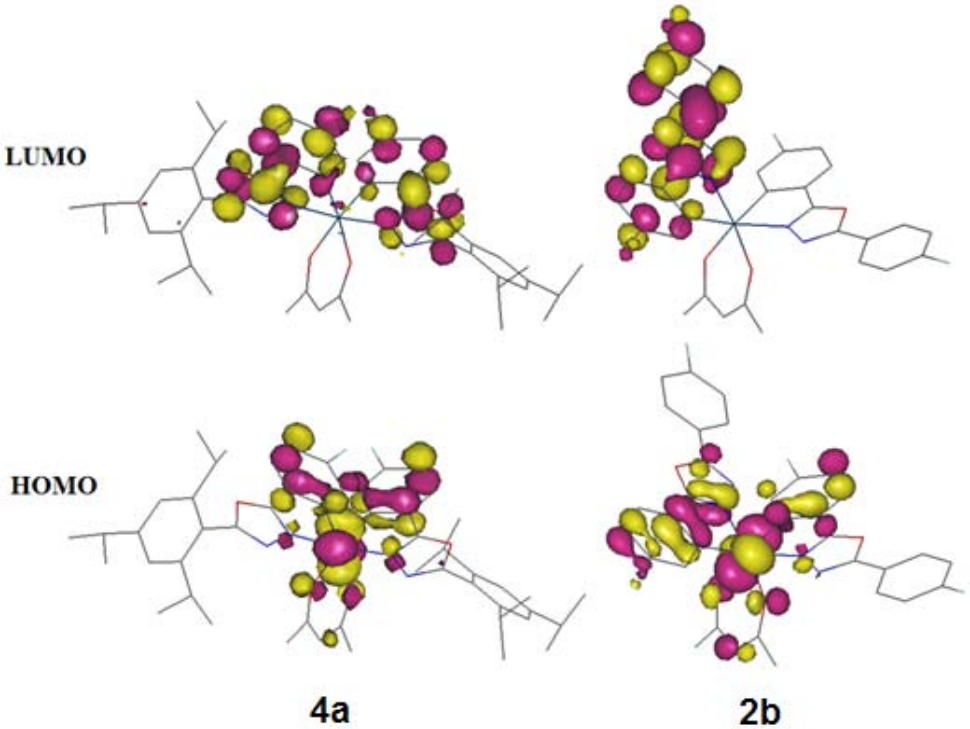

Fig. S1. HOMO and LUMO plots for N,N-*trans* Ir(*oxd*^{3})$_2$(*acac*) **(4a)** and N,N-*cis* Ir(*oxd*^{2})$_2$(*acac*) **(2b).**

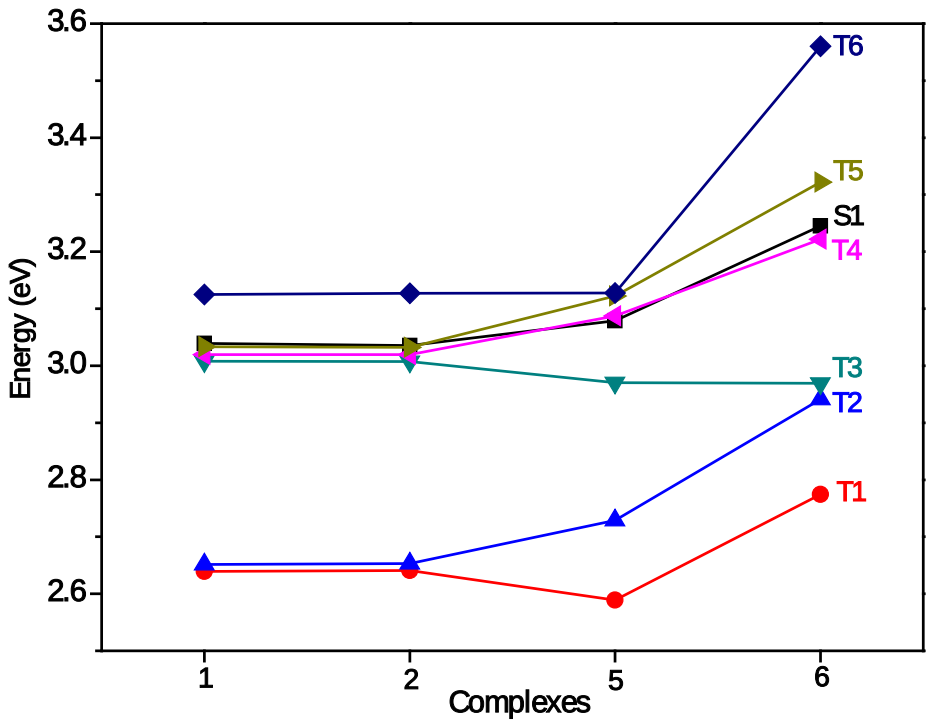

Fig. S2. Energy level diagram of the S_1 and T_1-T_6 states of complexes **2a**, **3a**, **3b** and **4b**.

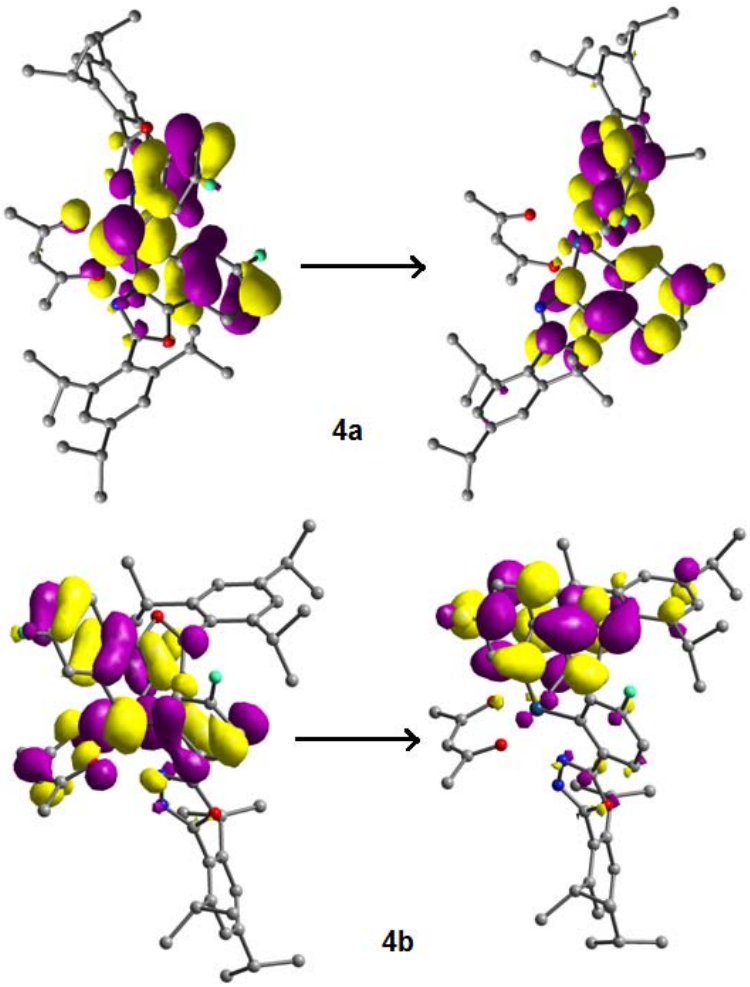

Figure S3. TD-CAM-B3LYP natural transition orbital (NTO) isodensity surfaces of **4a** and **4b** for the first vertical excitation: the hole (left) and electron (right) pair.

Optimized S_0 structure for N,N-*trans* Ir(oxd^0)$_2$($acac$) (1a)

C	-1.545461	-1.654753	-1.845731	C	5.920464	1.254731	-1.112452
C	-0.201898	-1.367398	-1.455326	H	5.134930	1.735084	-1.686474
C	0.794155	-2.057944	-2.164423	C	7.260294	1.542056	-1.353249
H	1.840598	-1.879868	-1.933375	H	7.525058	2.257285	-2.126773
C	0.472673	-2.962372	-3.178807	C	8.261922	0.915204	-0.605051
C	-0.859818	-3.220419	-3.533611	C	7.917158	-0.003499	0.388690
H	-1.090357	-3.926997	-4.325619	H	8.692046	-0.492401	0.972259
C	-1.881178	-2.559745	-2.863742	C	6.578351	-0.298586	0.638181
H	-2.922807	-2.735051	-3.120815	H	6.309319	-1.011837	1.410285
C	-2.478165	-0.895218	-1.069188	Ir	0.000000	0.033062	0.000000
C	-4.167354	0.038549	-0.129154	N	-2.043661	-0.074871	-0.133539
C	-5.572144	0.330133	0.112488	N	-3.119530	0.526533	0.471233
C	-5.920464	1.254732	1.112452	N	2.043661	-0.074871	0.133539
H	-5.134930	1.735084	1.686474	N	3.119530	0.526533	-0.471233
C	-7.260294	1.542057	1.353249	O	-3.825058	-0.867942	-1.114128
H	-7.525059	2.257285	2.126772	O	3.825058	-0.867942	1.114128
C	-8.261922	0.915205	0.605051	C	0.045186	2.842870	1.260328
C	-7.917158	-0.003499	-0.388691	C	-0.045186	2.842870	-1.260327
H	-8.692046	-0.492401	-0.972259	C	0.000001	3.467877	0.000000
C	-6.578351	-0.298586	-0.638182	H	0.000001	4.551765	0.000000
H	-6.309319	-1.011837	-1.410285	C	-0.067371	3.716816	-2.502344
C	1.545461	-1.654753	1.845731	H	-0.945214	3.467446	-3.109113
C	0.201898	-1.367398	1.455326	H	-0.084197	4.784452	-2.268418
C	-0.794155	-2.057944	2.164423	H	0.816605	3.498217	-3.112649
H	-1.840598	-1.879868	1.933375	C	0.067372	3.716816	2.502344
C	-0.472673	-2.962372	3.178807	H	0.084200	4.784452	2.268419
C	0.859818	-3.220419	3.533611	H	-0.816605	3.498219	3.112649
H	1.090357	-3.926997	4.325619	H	0.945214	3.467444	3.109114
C	1.881178	-2.559745	2.863742	O	0.070794	1.593047	1.502837
H	2.922806	-2.735050	3.120816	O	-0.070794	1.593047	-1.502837
C	2.478165	-0.895218	1.069188	H	-9.306870	1.142738	0.796520
C	4.167354	0.038549	0.129154	H	9.306870	1.142738	-0.796521
C	5.572144	0.330133	-0.112488	H	1.272346	-3.476517	-3.707761
				H	-1.272346	-3.476517	3.707761

Optimized T_1 structure for N,N-*trans* Ir(*oxd*^{0})$_2$(*acac*) (1a)

C	-1.458896	-1.647932	-1.833717
C	-0.125587	-1.347331	-1.426115
C	0.894381	-2.008746	-2.124435
H	1.933063	-1.813233	-1.876675
C	0.601958	-2.910617	-3.150772
C	-0.720606	-3.189034	-3.522332
H	-0.929150	-3.893784	-4.321873
C	-1.763507	-2.551932	-2.861113
H	-2.797973	-2.745305	-3.132512
C	-2.420877	-0.903487	-1.075047
C	-4.148258	0.026865	-0.204473
C	-5.562374	0.309824	-0.013871
C	-5.950666	1.236239	0.969568
H	-5.189106	1.723667	1.569313
C	-7.299784	1.516091	1.161964
H	-7.596036	2.232374	1.922872
C	-8.270357	0.879800	0.381544
C	-7.885675	-0.040772	-0.595744
H	-8.636692	-0.536841	-1.203797
C	-6.537271	-0.328434	-0.797068
H	-6.237378	-1.043118	-1.556367
C	1.594501	-1.739490	1.805991
C	0.204153	-1.396246	1.466589
C	-0.800175	-2.057255	2.170123
H	-1.841049	-1.822509	1.964966
C	-0.501837	-3.014675	3.149665
C	0.844975	-3.340847	3.451093
H	1.054582	-4.088443	4.212282
C	1.888989	-2.722960	2.798966
H	2.921593	-2.964544	3.032203
C	2.499366	-1.000644	1.073636
C	4.151100	0.039705	0.121114
C	5.502306	0.385587	-0.177719
C	5.784746	1.393293	-1.133994
H	4.960081	1.894016	-1.630263
C	7.099108	1.726597	-1.423563
H	7.305891	2.500347	-2.157997
C	8.159634	1.074171	-0.777021
C	7.887823	0.078465	0.168471
H	8.705958	-0.429322	0.672225
C	6.576946	-0.268788	0.471517
H	6.366112	-1.039681	1.204845
Ir	0.039424	0.032317	0.060433
N	-2.026026	-0.075799	-0.131203
N	-3.124856	0.526483	0.428171
N	2.028315	-0.059862	0.167090
N	3.038508	0.565862	-0.402507
O	-3.764309	-0.886276	-1.168501
O	3.875164	-0.956239	1.059603
C	-0.101969	2.786377	1.427722
C	-0.093544	2.895942	-1.090264
C	-0.167462	3.462587	0.196992
H	-0.253025	4.541864	0.244366
C	-0.107482	3.820565	-2.293816
H	-0.904593	3.515363	-2.980777
H	-0.249398	4.868998	-2.019676
H	0.839952	3.718466	-2.835783
C	-0.171417	3.596324	2.708704
H	-0.281239	4.668217	2.525462
H	-1.016359	3.245256	3.311908
H	0.736531	3.423841	3.297757
O	0.024600	1.530205	1.614261
O	-0.001535	1.659990	-1.380364
H	9.186761	1.340927	-1.008983
H	-9.322713	1.101365	0.535409
H	1.417417	-3.406043	-3.672584
H	-1.305306	-3.513964	3.683963

Optimized S_0 structure for N,N-*trans* Ir(*oxd*^{1})$_2$(*acac*) (2a)

C	-1.468208	-1.556570	-1.905493
C	-0.139115	-1.266575	-1.461498
C	0.890392	-1.948885	-2.123112
H	1.933438	-1.786996	-1.872362
C	0.588534	-2.845133	-3.142783
C	-0.712963	-3.123256	-3.568624
H	-0.877904	-3.834045	-4.370586
C	-1.757006	-2.462471	-2.936541
H	-2.784875	-2.643998	-3.238680
C	-2.431660	-0.798356	-1.169032
C	-4.159107	0.135360	-0.300940
C	-5.571563	0.425449	-0.118036
C	-5.962855	1.344529	0.872331
H	-5.203992	1.821042	1.483724
C	-7.307620	1.637468	1.064282
H	-7.632215	2.342459	1.822047
C	-8.254367	1.006122	0.260532
C	-7.895963	0.093049	-0.726028
H	-8.666286	-0.375330	-1.329109
C	-6.547441	-0.196677	-0.913886
H	-6.250009	-0.905851	-1.678842
C	1.468207	-1.556569	1.905494
C	0.139114	-1.266574	1.461498
C	-0.890393	-1.948883	2.123113
H	-1.933439	-1.786996	1.872362
C	-0.588535	-2.845131	3.142784
C	0.712961	-3.123254	3.568625
H	0.877902	-3.834043	4.370588
C	1.757004	-2.462470	2.936542
H	2.784874	-2.643996	3.238682
C	2.431659	-0.798356	1.169032
C	4.159107	0.135359	0.300940
C	5.571563	0.425448	0.118036
C	5.962855	1.344527	-0.872331
H	5.203992	1.821040	-1.483725
C	7.307620	1.637466	-1.064282
H	7.632216	2.342456	-1.822048
C	8.254367	1.006119	-0.260532
C	7.895963	0.093048	0.726029
H	8.666285	-0.375330	1.329111
C	6.547440	-0.196678	0.913887
H	6.250007	-0.905851	1.678844
Ir	0.000000	0.132968	0.000000
N	-2.037209	0.023803	-0.217470
N	-3.138070	0.625245	0.341779
N	2.037208	0.023802	0.217469
N	3.138070	0.625244	-0.341779
O	-3.775819	-0.772363	-1.270387
O	3.775818	-0.772363	1.270388
C	-0.008213	2.936552	1.260898
C	0.008219	2.936551	-1.260900
C	0.000005	3.561353	-0.000001
H	0.000007	4.645147	-0.000001
C	0.035266	3.808789	-2.503247
H	-0.819428	3.560562	-3.142643
H	0.011339	4.876499	-2.270833
H	0.941207	3.588137	-3.079591
C	-0.035258	3.808791	2.503244
H	-0.011324	4.876501	2.270830
H	-0.941202	3.588145	3.079587
H	0.819433	3.560559	3.142643
O	0.004844	1.685791	1.503474
O	-0.004844	1.685791	-1.503475
F	1.604512	-3.484018	-3.760312
F	-1.604514	-3.484016	3.760313
F	9.556677	1.288960	-0.444424
F	-9.556677	1.288963	0.444424

Optimized T_1 structure for N,N-*trans* Ir(*oxd*^{1})$_2$(*acac*) (2a)

C	-1.457935 -1.629573 -1.833882	C	5.925696 1.453966 -0.772532
C	-0.108292 -1.264360 -1.453915	H	5.158537 1.978498 -1.332032
C	0.947254 -1.891158 -2.122970	C	7.265253 1.769452 -0.953107
H	1.981118 -1.651977 -1.900345	H	7.576997 2.539902 -1.650356
C	0.673316 -2.833787 -3.108819	C	8.227154 1.076059 -0.218982
C	-0.631403 -3.200202 -3.467763	C	7.884184 0.078131 0.688175
H	-0.776641 -3.944609 -4.243809	H	8.664494 -0.436654 1.238645
C	-1.705665 -2.599550 -2.827026	C	6.540807 -0.235996 0.867485
H	-2.723816 -2.868108 -3.091136	H	6.257028 -1.011150 1.570927
C	-2.425170 -0.897442 -1.110087	Ir	0.000052 0.111722 -0.000068
C	-4.148484 0.132186 -0.317341	N	-2.031258 0.015759 -0.214715
C	-5.545905 0.446948 -0.140442	N	-3.108417 0.672792 0.273406
C	-5.925604 1.454025 0.772009	N	2.031365 0.015879 0.214600
H	-5.158454 1.978756 1.331336	N	3.108518 0.672812 -0.273694
C	-7.265169 1.769522 0.952506	O	-3.781152 -0.872781 -1.207244
H	-7.576929 2.540176 1.649521	O	3.781276 -0.872313 1.207382
C	-8.227058 1.075871 0.218606	C	-0.016780 2.954524 1.252417
C	-7.884067 0.077677 -0.688250	C	0.015957 2.954466 -1.252689
H	-8.664368 -0.437303 -1.238552	C	-0.000572 3.590008 -0.000151
C	-6.540683 -0.236461 -0.867483	H	-0.000803 4.673314 -0.000183
H	-6.256886 -1.011823 -1.570691	C	0.056479 3.801004 -2.508888
C	1.458090 -1.629016 1.834237	H	-0.805129 3.558019 -3.140848
C	0.108448 -1.263963 1.454164	H	0.053549 4.872258 -2.293122
C	-0.947080 -1.890552 2.123430	H	0.956550 3.552162 -3.082638
H	-1.980951 -1.651453 1.900752	C	-0.057650 3.801100 2.508575
C	-0.673110 -2.832880 3.109560	H	-0.055356 4.872346 2.292760
C	0.631616 -3.199172 3.468598	H	-0.957510 3.551768 3.082442
H	0.776878 -3.943341 4.244866	H	0.804172 3.558642 3.140447
C	1.705857 -2.598688 2.827666	O	0.003284 1.697228 1.467666
H	2.724017 -2.867140 3.091845	O	-0.003553 1.697156 -1.467875
C	2.425299 -0.897052 1.110230	F	1.701876 -3.426508 -3.752957
C	4.148600 0.132406 0.317200	F	-1.701654 -3.425418 3.753889
C	5.546018 0.447157 0.140221	F	9.527163 1.382841 -0.393936
		F	-9.527075 1.382664 0.393484

Optimized S_0 structure for N,N-*cis* Ir(*oxd*^{3})$_2$(*acac*) (4b)

Ir	-0.328056	-2.149827	-0.246479	C	5.658824	0.708396	0.350760
F	-3.503730	-6.569611	-0.552921	C	-4.353039	2.132685	-2.491646
F	-1.460084	-3.502056	4.922525	H	-3.673627	1.275375	-2.435235
O	-3.819335	-0.053622	-0.255438	C	-5.777855	1.577936	-2.690275
O	2.858490	-0.078120	1.506355	H	-6.068029	0.929200	-1.857325
O	0.939024	-3.777897	-0.400043	H	-6.511048	2.390731	-2.756436
O	-0.339184	-1.931378	-2.395332	H	-5.837168	0.993714	-3.616193
N	-1.732468	-0.677965	-0.159451	C	-3.906793	2.964873	-3.708797
N	-1.732830	0.695674	-0.062006	H	-4.576537	3.812285	-3.893893
N	1.453058	-0.905471	0.050401	H	-2.893807	3.358064	-3.571729
N	2.377516	-0.169314	-0.661320	H	-3.910627	2.340863	-4.609849
C	-2.974762	-1.100542	-0.275267	C	-5.371237	6.334469	0.141952
C	-2.981694	1.047313	-0.119974	H	-5.816800	6.528374	-0.843185
C	1.760908	-0.840998	1.323350	C	-6.507035	6.394023	1.181846
C	3.199755	0.314613	0.219440	H	-6.127345	6.225612	2.196594
C	2.353192	-5.398885	-1.321273	H	-6.991504	7.377537	1.166379
H	3.162325	-5.131111	-0.632513	H	-7.270130	5.634308	0.980376
H	1.799903	-6.224732	-0.859120	C	-4.325297	7.435516	0.400553
H	2.783958	-5.743080	-2.264506	H	-3.534255	7.417582	-0.357003
C	1.430045	-4.210872	-1.505142	H	-4.796596	8.425216	0.379646
C	1.200486	-3.722888	-2.797033	H	-3.851854	7.313749	1.381932
H	1.721104	-4.230976	-3.600196	C	-2.763891	2.606042	2.387277
C	0.360720	-2.650768	-3.172342	H	-2.613749	1.529965	2.256448
C	0.255136	-2.287742	-4.641493	C	-1.365166	3.241180	2.519164
H	0.588424	-1.253061	-4.781644	H	-1.436150	4.328870	2.642362
H	0.849560	-2.943832	-5.282238	H	-0.841752	2.834387	3.392496
H	-0.794069	-2.334861	-4.954142	H	-0.759303	3.035806	1.631059
C	-3.239794	-2.505444	-0.377602	C	-3.582342	2.788340	3.678930
C	-2.021460	-3.253770	-0.339825	H	-4.582934	2.352193	3.584405
C	-2.147924	-4.648065	-0.395467	H	-3.073689	2.293096	4.513874
H	-1.275848	-5.292476	-0.358902	H	-3.699144	3.844144	3.949311
C	-3.410254	-5.223783	-0.496228	C	2.809360	3.036663	-0.871721
C	-4.596151	-4.485466	-0.540013	H	2.053603	2.400648	-0.400988
H	-5.547657	-4.999621	-0.617987	C	2.577684	2.953116	-2.393736
C	-4.504959	-3.100914	-0.476920	H	2.652331	1.918148	-2.740503
H	-5.402827	-2.489290	-0.501804	H	1.579031	3.327696	-2.647919
C	-3.581972	2.390763	-0.048663	H	3.315515	3.555459	-2.938254
C	-4.246593	2.911954	-1.181953	C	2.576035	4.467182	-0.351178
C	-4.819175	4.183812	-1.084147	H	1.537742	4.764445	-0.538279
H	-5.339161	4.596315	-1.945003	H	2.760640	4.537525	0.726603
C	-4.736771	4.951242	0.080039	H	3.218711	5.201036	-0.851416
C	-4.060309	4.411266	1.179247	C	7.826918	3.732810	-0.588907
H	-3.985436	4.995916	2.091518	H	8.704808	3.159332	-0.261425
C	-3.484591	3.138257	1.150046	C	7.764149	5.010215	0.270238
C	0.975478	-1.511610	2.324463	H	6.914858	5.642002	-0.015501
C	-0.138234	-2.222595	1.777524	H	7.657898	4.768713	1.333477
C	-0.951359	-2.891459	2.703455	H	8.677686	5.603183	0.143811
H	-1.814702	-3.465337	2.384555	C	8.030310	4.075896	-2.077244
C	-0.653513	-2.843438	4.061766	H	7.193428	4.666076	-2.469079
C	0.436523	-2.149038	4.587093	H	8.945195	4.664638	-2.214184
H	0.615510	-2.149921	5.656630	H	8.113246	3.168866	-2.685856
C	1.261461	-1.473563	3.696450	C	5.889434	-0.697331	0.902976
H	2.122510	-0.919166	4.060016	H	4.958707	-1.263826	0.794820
C	4.370090	1.187899	0.023242	C	6.965334	-1.468366	0.114711
C	4.187858	2.490365	-0.503111	H	7.957943	-1.017066	0.225313
C	5.320738	3.284681	-0.698903	H	7.031480	-2.499194	0.481726
H	5.192616	4.281606	-1.110198	H	6.727272	-1.501892	-0.953887
C	6.608377	2.844467	-0.374486	C	6.226796	-0.653505	2.406627
C	6.750810	1.558885	0.152359	H	7.156590	-0.100378	2.585915
H	7.747835	1.206475	0.404225	H	5.428831	-0.164710	2.975144
				H	6.356742	-1.668136	2.801551

Optimized T_1 structure for N,N-*cis* Ir(*oxd*^{3})$_2$(*acac*) (4b)

Ir	-0.702175	-2.116931	-0.241701	C	5.625900	0.009121	0.369298
F	-4.456546	-6.065758	-0.385328	C	-4.565788	2.653897	-2.136995
F	-1.964692	-3.108069	4.967969	H	-4.057749	1.689662	-2.214840
O	-3.827787	0.492759	-0.215466	C	-6.059786	2.363247	-1.891385
O	2.728421	-0.370727	1.436044	H	-6.201014	1.792155	-0.968663
O	0.326401	-3.915275	-0.337833	H	-6.634958	3.293405	-1.807891
O	-0.714988	-2.049176	-2.404538	H	-6.478621	1.781972	-2.721602
N	-1.808482	-0.492019	-0.212292	C	-4.356178	3.369716	-3.485731
N	-1.593677	0.824574	-0.102339	H	-4.908710	4.314238	-3.543906
N	1.259738	-1.107462	-0.004695	H	-3.296930	3.587079	-3.661337
N	2.286007	-0.544664	-0.734334	H	-4.712252	2.732337	-4.303482
C	-3.192155	-0.729945	-0.271684	C	-4.031605	7.064457	0.262333
C	-2.775663	1.404294	-0.113494	H	-4.735479	7.286079	-0.551437
C	1.548452	-0.999548	1.268196	C	-4.736605	7.409848	1.588157
C	3.146033	-0.110467	0.137201	H	-4.080509	7.230361	2.448034
C	1.525934	-5.754277	-1.153546	H	-5.025875	8.467353	1.605358
H	2.373797	-5.547828	-0.490558	H	-5.640140	6.805982	1.725564
H	0.878424	-6.468894	-0.632468	C	-2.787651	7.948870	0.049963
H	1.894166	-6.211928	-2.074635	H	-2.305526	7.732210	-0.909596
C	0.760379	-4.473185	-1.411114	H	-3.063037	9.010217	0.062170
C	0.587537	-4.032515	-2.726902	H	-2.045219	7.788571	0.840822
H	1.030240	-4.644619	-3.503518	C	-1.569761	3.032275	2.078104
C	-0.123101	-2.888202	-3.151410	H	-1.640659	1.943055	2.033645
C	-0.220683	-2.596303	-4.635700	C	-0.103065	3.398145	1.775179
H	0.174078	-1.593446	-4.832895	H	0.046509	4.484794	1.796071
H	0.322706	-3.323043	-5.244580	H	0.564764	2.951061	2.521716
H	-1.274655	-2.593915	-4.936196	H	0.192075	3.029838	0.787722
C	-3.644689	-2.023953	-0.296736	C	-1.959061	3.447255	3.509855
C	-2.526035	-2.986018	-0.278572	H	-3.006934	3.209887	3.723854
C	-2.836120	-4.332844	-0.308866	H	-1.335073	2.909998	4.233500
H	-2.058392	-5.089158	-0.286191	H	-1.813183	4.518927	3.687895
C	-4.178776	-4.741599	-0.357160	C	3.134126	2.516917	-1.227825
C	-5.256471	-3.836511	-0.369008	H	2.285798	2.040315	-0.726944
H	-6.269025	-4.226619	-0.400940	C	2.958274	2.267614	-2.739830
C	-5.006024	-2.481503	-0.336994	H	2.916920	1.195840	-2.954990
H	-5.820300	-1.763962	-0.340699	H	2.026237	2.723094	-3.094745
C	-3.080857	2.832320	-0.020633	H	3.788407	2.704116	-3.309055
C	-3.957257	3.428149	-0.966837	C	3.057112	4.019805	-0.902374
C	-4.249541	4.787921	-0.835768	H	2.068135	4.405457	-1.174500
H	-4.922388	5.252411	-1.551968	H	3.212828	4.208708	0.165583
C	-3.693459	5.583027	0.168632	H	3.797281	4.604453	-1.460858
C	-2.818575	4.974942	1.074814	C	8.171894	2.690733	-0.659768
H	-2.377332	5.576892	1.863943	H	8.962253	2.048023	-0.248723
C	-2.504339	3.615602	1.018665	C	8.205545	4.019864	0.119308
C	0.677729	-1.514715	2.293679	H	7.447449	4.718860	-0.253323
C	-0.507476	-2.125971	1.783192	H	8.016104	3.859383	1.186303
C	-1.391674	-2.664229	2.725567	H	9.184389	4.502854	0.014696
H	-2.306786	-3.159330	2.420494	C	8.487967	2.914143	-2.150957
C	-1.094299	-2.580859	4.082933	H	7.743143	3.565048	-2.623845
C	0.061823	-1.978247	4.578437	H	9.468263	3.390871	-2.268317
H	0.237936	-1.945900	5.648017	H	8.500450	1.966533	-2.700310
C	0.958998	-1.438187	3.664159	C	5.670039	-1.363027	1.040107
H	1.872908	-0.962900	4.009371	H	4.685734	-1.830195	0.931789
C	4.419410	0.598463	-0.073501	C	6.679408	-2.311015	0.364559
C	4.416874	1.860369	-0.719697	H	7.712369	-1.966739	0.488190
C	5.642682	2.504622	-0.905179	H	6.611469	-3.310036	0.810725
H	5.653756	3.469403	-1.403277	H	6.480962	-2.402852	-0.708672
C	6.851702	1.957334	-0.462335	C	5.952649	-1.234941	2.550079
C	6.817500	0.713742	0.171651	H	6.935217	-0.782770	2.730668
H	7.752645	0.276702	0.512598	H	5.199452	-0.609661	3.040737
				H	5.943404	-2.221654	3.028286