Supporting Information

Combined Effects of Stereoisomeric and Steric Factors on Electronic and Photophysical Properties of *Bis*-cyclometalated Ir(III) Complexes Containing 2,5-Diaryl-1,3,4-oxadiazole Based and Picolinate Ligands

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Table S1. Highest occupied and lowest virtual orbitals for N,N-cis of $Ir(oxd^1)_2(pic)$, $Ir(oxd^2)_2(pic)$ and $Ir(oxd^3)_2(pic)$: character and energies.

MO	E_{MO} (eV)	Ir	Oxd[a]	pic	Oxd[b]	Character
$Ir(oxd^1)_2(pic)$						
L+3	-0.87	1	2	95	2	□ (pic)*
L+2	-1.27	3	87	6	4	□ (oxd)*
L+1	-1.39	2	3	86	9	□ (pic)*
LUMO	-1.49	3	6	8	83	□ (oxd)*
HOMO	-5.43	44	28	8	20	5d (44%) + □ (oxd)
H-1	-5.76	44	19	29	9	5d (44%) + □ (pic)
H-2	-6.05	4	5	85	6	□ (pic)
H-3	-6.07	34	11	10	46	5d (34%+□ (oxd)
$Ir(oxd^2)_2(pic)$						
L+3	-0.85	1	2	92	4	□ (pic)*
L+2	-1.27	3	82	11	4	□ (oxd)*
L+1	-1.38	2	9	84	5	□ (pic)*
LUMO	-1.51	3	6	4	88	□ (oxd)*
HOMO	-5.43	44	28	8	20	5d (44%) + □ (oxd)
H-1	-5.74	44	18	29	9	5d (44%) + □ (pic)
H-2	-6.04	23	3	48	26	□ (pic + oxd)
H-3	-6.05	15	11	49	25	□ (pic + oxd)
$Ir(oxd^3)_2(pic)$						
L+3	-1.10	4	11	2	84	□ (oxd)*
L+2	-1.36	2	1	97	1	□ (pic)*
L+1	-1.78	1	88	0	11	□ (oxd)*
LUMO	-1.87	1	11	1	88	□ (oxd)*
HOMO	-5.46	42	30	10	18	5d (42%) + □ (oxd)
H-1	-5.70	39	19	27	15	5d (39%) + □ (oxd)
H-2	-5.98	2	3	90	5	□ (pic)
H-3	-6.02	29	11	10	50	5d (29%) + □ (oxd)

Table S2. Highest occupied and lowest virtual orbitals for N,N-*trans* isomers of $Ir(oxd^1)_2(pic)$, $Ir(oxd^2)_2(pic)$ and $Ir(oxd^3)_2(pic)$: character and energies.

MO	E_{MO} (eV)	Ir	Oxd[a]	pic	Oxd[b]	Character
$Ir(oxd^1)_2(pic)$						
L+3	-0.95	1	1	96	2	□ (pic)*
L+2	-1.15	2	4	2	91	□ (oxd)*
L+1	-1.39	4	82	12	3	□ (oxd)*
LUMO	-1.51	2	10	86	2	□ (pic)*
HOMO	-5.46	45	20	5	30	5d (45%) + □ (oxd)
H-1	-5.73	47	16	21	16	5d (47%) + □ (oxd+pic)
H-2	-5.85	48	29	11	11	5d (48%) +□ (oxd)
H-3	-6.17	9	17	17	57	□ (oxd + pic)
$Ir(oxd^2)_2(pic)$						
L+3	-0.94	1	1	97	1	□ (pic)*
L+2	-1.17	2	3	2	94	□ (oxd)*
L+1	-1.43	3	59	37	1	□ (oxd)*
LUMO	-1.50	1	36	60	3	□ (pic+oxd)*
HOMO	-5.43	45	19	5	30	5d (45%) + □ (oxd)
H-1	-5.68	46	16	21	17	5d (46%) + □ (oxd+pic)
H-2	-5.83	48	30	11	11	5d (48%) +□ (oxd)
H-3	-6.13	10	15	18	57	□ (oxd + pic)
$Ir(oxd^3)_2(pic)$						
L+3	-1.11	4	91	2	2	□ (oxd)*
L+2	-1.51	2	1	94	3	□ (pic)*
L+1	-1.65	0	1	3	96	□ (oxd)*
LUMO	-1.91	1	98	1	1	□ (oxd)*
HOMO	-5.47	41	21	5	33	5d (41%) + □ (oxd)
H-1	-5.70	42	18	18	22	5d (42%) + □ (oxd)
H-2	-5.89	48	30	11	11	5d (48%) + □ (oxd)
H-3	-6.12	14	16	19	51	5d (14%) + □ (oxd)

Table S3. Highest occupied and lowest virtual orbitals character (and energies) for N,N-cis isomer of Ir(oxd^3)$_2$(pic) as function of torsional angle.

MO	E_{MO} (eV)	oxd[a]	Ir	pic	oxd[b]	Character
. □'□$_a$ = 66.6° and □$_b$ = 67°						
L+3	-1.04	95	2	0	3	□* (oxd)
L+2	-1.26	**4**	1	1	93	□* (oxd)
L+1	-1.47	**18**	3	79	1	□* (pic)
LUMO	-1.57	**78**	2	19	2	□* (oxd)
HOMO	-5.47	19	45	6	31	5d(45%)+ □ (oxd)
H-1	-5.70	16	47	22	16	5d(47%)+ □ (oxd+pic)
H-2	-5.86	30	48	11	11	5d(48%)+ □ (oxd)
H-3	-6.17	14	9	19	59	□ (oxd+pic)
. □''□$_a$ =76.5° and □$_b$ = 88.5°						
L+3	-1.03	98	1	0	1	□* (oxd)
L+2	-1.18	**5**	2	**1**	92	□* (oxd)
L+1	-1.44	**57**	4	**38**	2	□* (oxd + pic)
LUMO	-1.52	**36**	1	**60**	3	□* (pic + oxd)
HOMO	-5.47	19	45	6	31	5d(45%)+ □ (oxd)
H-1	-5.70	16	47	22	14	5d(47%)+ □ (oxd+pic)
H-2	-5.85	30	48	11	11	5d(48%)+ □ (oxd)
H-3	-6.18	14	8	19	60	□ (oxd+pic)

□'□$_a$ and □$_b$ kept constant (66.6° and 67°, respectively) and equal to those for Ir(oxd^2)$_2$(pic), while in □''□$_a$ and □$_b$ kept constant (76.5° and 88.5°, respectively)and equal to those for Ir(oxd^1)$_2$(pic).

Table S4: TD-DFT transition electric dipole moment (μ_{S1} in D), singlet-triplet splitting (ΔS_1-Tn in eV), and DFT Zero-field splitting (ZFS in cm^{-1}).

	1	**2**	**3**	**3' (3")** [a]	**4**	**5**	**6**
ΔST_1 (eV)	0.474	0.478	0.489	0.497 (0.489)	0.413	0.417	0.450
ΔST_2	0.340	0.331	0.350	0.342 (0.337)	0.378	0.377	0.429
ΔST_3	0.081	0.069	0.109	0.061 (0.068)	0.002	0.004	0.044
ΔST_4	-0.034	-0.036	-0.009	-0.020(-0.014)	-0.046	-0.050	-0.011
ΔST_5			-0.044	-0.029(-0.030)	-0.070	-0.077	-0.077
ΔST_6			-0.049	-0.153(-0.155)	-0.224	-0.220	-0.087
MLCT							
Δ_{S1} (D)	0.26	0.32	2.03	0.40 (0.28)	1.24	1.32	2.71
ZFS (cm^{-1})[b]		0.34	0.09				-0.13
Φ_{PL} (%)	< 1 [c]	< 1 [c]					

[a] Hypothetical structures obtained by optimizing **3**, keeping frozen the ligand torsional angles at their respective values in **1** (for **3'**) and **2** (for **3''**). [b] The ZFS values are given relative to the ZFS of **6**. [c] Chen, L.; You, H.; Yang, C.; Ma D.; and Qin, J. Chem. Commun. 2007, 1352–1354. [d] Zheng, Y.; Batsanov, A. S. and Bryce. M. R. *Inorg. Chem*. **2011**, 50, 3354–3362.

Table S5: Calculated excited energies, dominant orbital excitations, and oscillator strength (*f*) from TDDFT calculations for the N,N-*cis* series.

Cplx	St.	E_{th}	$\lambda_{cal.}$	*f*	Excitation (contribution)	Character
1	S_1	3.32	373	0.021	H->L (96%)	MLCT/LLCT
	S_2	3.38	367	0.038	H->L+1 (93%)	MLCT/LLCT/ILCT
	S_3	3.58	346	0.059	H->L+2 (94%)	MLCT/LLCT/ILCT
	S_4	3.64	340	0.078	H-1->L (75%)	MLCT/LLCT/ILCT
	S_5	3.69	336	0.007	H-2->L (93%)	MLCT/LLCT
	S_6	3.72	334	0.022	H-2->L+1 (24%), H-1->L+1 (49%)	MLCT/LLCT/ILCT
	S_7	3.84	323	0.066	H-2->L+1 (64%), H-1->L+1 (27%)	MLCT/LLCT/ILCT
	S_8	3.90	318	0.020	H-1->L+2 (90%)	MLCT/LLCT/ILCT
	S_9	4.01	309	0.024	H-2->L+2 (70%)	MLCT/LLCT
	S_{10}	4.02	308	0.001	H->L+3 (73%)	MLCT/LLCT
	T_1	2.85	436		H->L+1 (56%)	MLCT/LLCT/ILCT
	T_2	2.98	416		H-1->L+2 (19%), H->L+2 (39%)	MLCT/LLCT/ILCT
	T_3	3.24	383		H->L (64%)	MLCT/LLCT
2	S_1	3.30	376	0.026	H->L (97%)	MLCT/LLCT/ILCT
	S_2	3.36	369	0.047	H->L+1 (94%)	MLCT/LLCT/ILCT
	S_3	3.56	348	0.068	H->L+2 (93%)	MLCT/LLCT/ILCT
	S_4	3.62	343	0.080	H-1->L (77%)	MLCT/LLCT/ILCT
	S_5	3.68	337	0.005	H-2->L (83%)	MLCT/LLCT/ILCT
	S_6	3.69	336	0.031	H-1->L+1 (54%)	MLCT/LLCT/ILCT
	S_7	3.82	324	0.057	H-2->L+1 (72%)	MLCT/LLCT/ILCT
	S_8	3.88	319	0.030	H-1->L+2 (90%)	MLCT/LLCT/ILCT
	S_9	4.00	310	0.018	H->L+3 (71%)	MLCT/LLCT/ILCT
	S_{10}	4.01	310	0.007	H-2->L+2 (68%)	MLCT/LLCT
	T_1	2.82	440		H->L (17%), H->L+1 (51%)	MLCT/LLCT/ILCT
	T_2	2.97	418		H-1->L+2 (22%), H->L+2 (38%)	MLCT/LLCT/ILCT
	T_3	3.23	384		H->L (61%)	MLCT/LLCT
3	S_1	3.18	390	0.158	H->L (92%)	MLCT/LLCT/ILCT
	S_2	3.29	377	0.036	H->L+1 (54%), H->L+2 (41%)	MLCT/LLCT/ILCT
	S_3	3.35	370	0.110	H->L+1 (40%), H->L+2 (53%)	MLCT/LLCT/ILCT
	S_4	3.45	360	0.066	H-1->L (90%)	MLCT/LLCT/ILCT
	S_5	3.61	344	0.110	H-2->L (43%), H-1->L+1 (38%)	MLCT/LLCT/ILCT
	S_6	3.62	343	0.031	H-2->L (42%), H-1->L+1 (27%)	MLCT/LLCT/ILCT
	S_7	3.67	338	0.056	H-1->L+1 (28%), H-1->L+2 (61%)	MLCT/LLCT/ILCT
	S_8	3.72	333	0.011	H-2->L+1 (22%), H-2->L+2 (62%)	MLCT/LLCT
	S_9	3.80	327	0.026	H-2->L+1 (62%), H-2->L+2 (25%)	MLCT/LLCT
	S_{10}	3.84	323	0.066	H->L+3 (79%)	MLCT/LLCT/ILCT
	T_1	2.63	471		H->L (61%)	MLCT/LLCT
	T_2	2.74	452		H-1->L+1 (30%), H->L+1 (31%)	MLCT/LLCT/ILCT
	T_3	3.11	398		H-9->L (10%), H->L+3 (39%)	MLCT/LLCT/ILCT

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

Cpl	St	E_{th}	$\lambda_{cal.}$	*f*	Excitation (contribution)	Character
4	S_1	3.28	378	0.100	H->L (90%)	MLCT/LLCT/ILCT
	S_2	3.39	366	0.010	H->L+1 (92%)	MLCT/LLCT
	S_3	3.43	361	0.010	H->L+2 (91%)	MLCT/LLCT/ILCT
	S_4	3.70	335	0.022	H-1->L (81%	MLCT/LLCT
	S_5	3.80	326	0.036	H-1->L+1 (80%)	MLCT/LLCT/ILCT
	S_6	3.90	318	0.033	H-1->L+2 (76%)	MLCT/LLCT/ILCT
	S_7	3.94	315	0.052	H-2->L (69%)	LLCT
	S_8	4.03	308	0.042	H-2->L+2 (67%)	LLCT
	S_9	4.04	307	0.010	H->L+3 (80%)	MLCT/LLCT
	S_{10}	3.28	305	0.047	H-2->L+1 (43%)	ILCT
	T_1	2.87	432		H-1->L+2 (11%), H->L (49%)	MLCT/LLCT/ILCT
	T_2	2.90	427		H-1->L (15%),H->L+2 (32%)	MLCT/LLCT/ILCT
	T_3	3.28	378		H-2->L (30%), H->L (27%)	MLCT/LLCT/ILCT
5	S_1	3.27	379	0.106	H->L (92%)	MLCT/LLCT/ILCT
	S_2	3.39	366	0.001	H->L+1 (94%)	MLCT/LLCT
	S_3	3.45	359	0.010	H->L+2 (92%)	MLCT/LLCT/ILCT
	S_4	3.68	337	0.025	H-1->L (84%)	MLCT/LLCT
	S_5	3.78	328	0.046	H-1->L+1 (83%)	MLCT/LLCT/ILCT
	S_6	3.88	320	0.022	H-2->L (22%), H-1->L+2 (62%)	MLCT/LLCT/ILCT
	S_7	3.92	317	0.069	H-2->L (60%), H-1->L+2 (27%)	MLCT/LLCT/ILCT
	S_8	4.02	309	0.028	H-2->L+1 (38%), H-2->L+2 (45%)	MLCT/LLCT/ILCT
	S_9	4.03	308	0.055	H-2->L+1 (32%), H-2->L+2 (35%)	MLCT/LLCT/ILCT
	S_{10}	4.05	306	0.025	H->L+3 (75%)	MLCT/LLCT
	T_1	2.86	434		H->L (51%)	MLCT/LLCT/ILCT
	T_2	2.90	428		H-1->L (18%), H->L+2 (31%)	MLCT/LLCT/ILCT
	T_3	3.27	379		H-2->L (33%), H->L (30%)	MLCT/LLCT/ILCT
6	S_1	3.12	398	0.207	H->L (93%)	MLCT/LLCT/ILCT
	S_2	3.23	384	0.016	H->L+1 (94%)	MLCT/ILCT
	S_3	3.41	364	0.003	H->L+2 (97%)	MLCT/LLCT
	S_4	3.46	358	0.055	H-1->L (86%)	MLCT/LLCT
	S_5	3.57	347	0.177	H-1->L+1 (87%)	MLCT/LLCT/ILCT
	S_6	3.72	334	0.114	H-2->L (82%)	LLCT
	S_7	3.75	331	0.043	H-1->L+2 (87%)	MLCT/LLCT/ILCT
	S_8	3.79	327	0.084	H-2->L+1 (85%)	LLCT
	S_9	3.83	324	0.103	H->L+3 (83%)	MLCT/LLCT/ILCT
	S_{10}	3.90	318	0.011	H->L+4 (89%)	
	T_1	2.67	465		H-1->L+1 (27%), H->L (33%)	MLCT/LLCT/ILCT
	T_2	2.69	461		H-1->L (31%), H->L+1 (23%)	MLCT/LLCT/ILCT
	T_3	3.07	404		H->L (25%), H->L+3 (20%)	MLCT/LLCT/ILCT

Table S7: XYZ coordinates of the optimized S_0 structure for **(1)**

Ir	-0.027260	-2.186367	-0.139803	C	-2.833260 -3.067687 -0.295746
F	-1.501525	-3.231558	5.028994	C	-1.497751 -3.576971 -0.235092
F	-2.339690	-7.113117	-0.316562	C	-1.359565 -4.971711 -0.240508
O	1.511193	-3.576104	-0.140048	H	-0.381187 -5.436729 -0.177690
O	3.029473	-4.597829	-1.451236	C	-2.493596 -5.773705 -0.310675
O	2.798691	0.284134	1.679602	C	-3.797457 -5.269439 -0.372048
O	-3.859957	-0.766635	-0.237538	H	-4.636300 -5.954758 -0.422218
N	0.406929	-2.345920	-2.263073	C	-3.966979 -3.892181 -0.362146
N	1.516268	-0.681446	0.201313	H	-4.962999 -3.459563 -0.401807
N	2.443477	0.060292	-0.499010	C	-4.121029 1.666751 -0.105557
N	-1.688174	-0.981977	-0.216594	C	-4.570022 2.273070 -1.316477
N	-1.952135	0.371063	-0.157282	C	-4.560115 2.135516 1.164042
C	2.073309	-3.851273	-1.285375	C	-5.527937 3.284763 -1.207636
C	1.448677	-3.170745	-2.493703	C	-5.521132 3.157931 1.175264
C	1.938575	-3.390441	-3.778632	C	-6.038562 3.730410 0.015188
H	2.780084	-4.064591	-3.890610	H	-5.900035 3.749356 -2.109079
C	1.334585	-2.741409	-4.852215	H	-5.881557 3.515351 2.126242
H	1.695387	-2.894443	-5.865362	C	-3.992586 1.944503 -2.725150
C	0.257783	-1.887288	-4.604508	C	-2.528415 2.451338 -2.793284
H	-0.241389	-1.358501	-5.409967	C	-4.041319 0.435823 -3.076316
C	-0.176191	-1.714237	-3.293601	C	-4.771625 2.665598 -3.851017
H	-1.002071	-1.056141	-3.046188	H	-2.488833 3.535128 -2.634289
C	1.750609	-0.539208	1.484130	H	-1.891030 1.976804 -2.043402
C	3.194906	0.625882	0.395244	H	-2.106021 2.242526 -3.784544
C	-2.834783	-1.635817	-0.259285	H	-5.027545 0.005098 -2.872704
C	-3.245525	0.477707	-0.167906	H	-3.833701 0.307444 -4.144954
C	0.954622	-1.214358	2.473857	H	-3.295738 -0.154258 -2.541381
C	-0.033040	-2.075034	1.903450	H	-4.330619 2.393704 -4.815823
C	-0.857448	-2.748854	2.813940	H	-5.828199 2.374613 -3.876074
H	-1.629361	-3.433928	2.480984	H	-4.712803 3.755730 -3.769885
C	-0.685491	-2.566043	4.183541	C	-7.119541 4.827911 0.037268
C	0.286084	-1.729891	4.732085	C	-7.556259 5.197668 1.467625
H	0.373295	-1.633335	5.808618	C	-6.573391 6.106143 -0.643210
C	1.118727	-1.045225	3.855421	C	-8.366483 4.329235 -0.732560
H	1.890061	-0.382190	4.237576	H	-7.976189 4.338147 2.002184
C	2.715057	3.518889	-0.365169	H	-6.724446 5.597090 2.059075
C	2.200724	3.087798	-1.762198	H	-8.331343 5.971086 1.426082
H	1.218910	3.539590	-1.954174	H	-6.290541 5.927004 -1.685740
H	2.888188	3.428881	-2.545400	H	-7.335615 6.894683 -0.636225
H	2.101243	2.003562	-1.842965	H	-5.689572 6.483437 -0.116196
C	1.677795	3.135391	0.723341	H	-9.144970 5.101826 -0.736564
H	2.090538	3.257379	1.731116	H	-8.133230 4.085908 -1.774462

H	0.806340	3.794109	0.638147	H	-8.783234	3.430006	-0.264533
H	1.297933	2.118562	0.621350	C	-3.975439	1.656951	2.527205
C	2.770561	5.067174	-0.362126	C	-3.970927	0.115573	2.700088
H	3.172681	5.464885	0.576991	C	-2.528470	2.199067	2.659054
H	3.360574	5.471745	-1.190745	C	-4.778939	2.216473	3.725901
H	1.753509	5.455587	-0.480780	H	-4.926801	-0.329101	2.402880
C	4.349538	1.529445	0.223240	H	-3.168326	-0.378312	2.150677
C	4.120485	2.892764	-0.116127	H	-3.804091	-0.126868	3.755255
C	5.244167	3.717792	-0.269512	H	-2.522959	3.295010	2.630865
H	5.092289	4.753816	-0.526027	H	-2.098174	1.882230	3.617059
C	6.550666	3.264025	-0.101554	H	-1.879308	1.834487	1.859680
C	6.727685	1.919622	0.234033	H	-4.336515	1.837484	4.652922
H	7.738542	1.561253	0.363905	H	-4.747346	3.309395	3.782031
C	5.670694	1.019776	0.404476	H	-5.828059	1.898944	3.705541
C	7.779019	4.178483	-0.271511	C	6.023191	-0.440644	0.827294
C	7.392853	5.624914	-0.635668	C	5.888144	-0.563940	2.366913
H	8.299419	6.230588	-0.746236	C	5.157156	-1.527527	0.140061
H	6.846064	5.675721	-1.584196	C	7.491151	-0.790609	0.470025
H	6.776958	6.092676	0.140956	H	6.560398	0.138155	2.874125
C	8.580789	4.214985	1.051890	H	4.869695	-0.360929	2.705783
H	8.931722	3.220272	1.345687	H	6.154141	-1.579295	2.685752
H	9.461121	4.860406	0.944537	H	5.079703	-1.362602	-0.939444
H	7.968163	4.609111	1.870850	H	5.621142	-2.507234	0.293791
C	8.679627	3.623931	-1.401435	H	4.148188	-1.612611	0.544042
H	9.026302	2.607797	-1.186805	H	7.669798	-1.844891	0.703777
H	8.140792	3.598787	-2.355540	H	7.697658	-0.644985	-0.596501
H	9.565072	4.258969	-1.527325	H	8.221034	-0.213724	1.046813

Table S8: XYZ coordinates of the optimized T_1 structure for **(1)**

Ir	0.008215	-2.256030	-0.149384	C	-2.825946 -3.028463 -0.456203
F	-1.697065	-3.435901	4.916670	C	-1.517510 -3.596713 -0.369147
F	-2.499512	-7.084341	-0.657550	C	-1.436269 -4.992902 -0.440052
O	1.470921	-3.709339	-0.105375	H	-0.482985 -5.505039 -0.357970
O	2.932624	-4.863351	-1.367630	C	-2.598945 -5.742006 -0.592762
O	2.615570	0.362518	1.792432	C	-3.877041 -5.179643 -0.677394
O	-3.768158	-0.697483	-0.325701	H	-4.740992 -5.824853 -0.791875
N	0.538446	-2.403619	-2.268548	C	-3.989746 -3.798451 -0.605834
N	1.476314	-0.798939	0.241894	H	-4.964509 -3.321503 -0.660503
N	2.403261	-0.077477	-0.402376	C	-3.951800 1.734684 -0.090090
N	-1.608388	-0.987587	-0.259305	C	-4.349342 2.404271 -1.285559
N	-1.826403	0.368635	-0.141405	C	-4.409638 2.163149 1.187103
C	2.044096	-4.033276	-1.235312	C	-5.279652 3.439205 -1.158589
C	1.528289	-3.297414	-2.461215	C	-5.340646 3.212592 1.216521
C	2.062266	-3.538761	-3.724737	C	-5.810320 3.847837 0.068771
H	2.856857	-4.271424	-3.808053	H	-5.613225 3.952569 -2.048750
C	1.558536	-2.834520	-4.815121	H	-5.716592 3.540606 2.172055
H	1.955812	-3.001254	-5.812316	C	-3.741619 2.118446 -2.690745
C	0.535066	-1.907535	-4.605956	C	-2.266892 2.598100 -2.698550
H	0.115235	-1.334333	-5.426104	C	-3.805715 0.625884 -3.103539
C	0.051338	-1.719633	-3.314487	C	-4.477195 2.898178 -3.806604
H	-0.737056	-1.007335	-3.096232	H	-2.210645 3.673399 -2.493503
C	1.597847	-0.556249	1.608651	H	-1.661112 2.079666 -1.951348
C	3.069658	0.600415	0.508294	H	-1.819960 2.420698 -3.685249
C	-2.774138	-1.600164	-0.359881	H	-4.800000 0.200120 -2.931697
C	-3.114415	0.521100	-0.181823	H	-3.584223 0.538214 -4.173513
C	0.828800	-1.236833	2.512773	H	-3.073640 0.005447 -2.583942
C	-0.122584	-2.194424	1.877891	H	-4.018317 2.653780 -4.770422
C	-0.951520	-2.904149	2.725012	H	-5.538596 2.630980 -3.867405
H	-1.664923	-3.626515	2.343282	H	-4.398306 3.982863 -3.682374
C	-0.873776	-2.722846	4.116986	C	-6.860342 4.974468 0.109900
C	0.030622	-1.825179	4.731213	C	-7.334221 5.287872 1.541984
H	0.034566	-1.745625	5.814008	C	-6.255438 6.266803 -0.489601
C	0.879209	-1.082933	3.950521	C	-8.094678 4.551046 -0.722591
H	1.585322	-0.387900	4.392809	H	-7.791411 4.415000 2.021486
C	2.528471	3.361393	-0.628936	H	-6.513350 5.638621 2.177842
C	2.104312	2.762077	-1.993505	H	-8.089261 6.081419 1.513098
H	1.115177	3.144127	-2.277785	H	-5.943407 6.129007 -1.530130
H	2.815575	3.050217	-2.776966	H	-6.994554 7.076820 -0.468489
H	2.056248	1.671812	-1.960697	H	-5.379021 6.591570 0.082805

C	1.450195	3.057846	0.444436	H	-8.850886	5.345276	-0.711108
H	1.807713	3.302716	1.450716	H	-7.835070	4.353815	-1.767944
H	0.562716	3.669508	0.246781	H	-8.550653	3.642046	-0.313865
H	1.110281	2.022296	0.440101	C	-3.878291	1.607783	2.542926
C	2.532262	4.902375	-0.792929	C	-3.938687	0.061907	2.651715
H	2.881701	5.412414	0.112255	C	-2.415576	2.086144	2.733968
H	3.143143	5.238000	-1.637115	C	-4.690351	2.150329	3.743625
H	1.509092	5.238499	-0.991608	H	-4.905597	-0.330786	2.318784
C	4.194093	1.531491	0.302647	H	-3.145594	-0.441988	2.097707
C	3.939029	2.824649	-0.238966	H	-3.802553	-0.230084	3.698736
C	5.039488	3.669174	-0.446863	H	-2.365775	3.181279	2.744469
H	4.865662	4.648960	-0.861593	H	-2.026278	1.719644	3.691775
C	6.347339	3.308696	-0.131900	H	-1.756212	1.722906	1.942467
C	6.550054	2.039266	0.414842	H	-4.284574	1.719935	4.664894
H	7.562109	1.754795	0.663520	H	-4.620259	3.238423	3.842921
C	5.520646	1.121573	0.643780	H	-5.749458	1.872901	3.687170
C	7.549730	4.244638	-0.358306	C	5.902913	-0.250752	1.279348
C	7.138779	5.597083	-0.971491	C	5.639741	-0.193250	2.805708
H	8.027930	6.222680	-1.109415	C	5.149216	-1.456011	0.660973
H	6.666207	5.474555	-1.952767	C	7.410421	-0.560151	1.090594
H	6.446817	6.147223	-0.323603	H	6.228264	0.606822	3.270178
C	8.246230	4.523547	0.995375	H	4.586144	-0.014703	3.029316
H	8.603520	3.603114	1.468637	H	5.932001	-1.142756	3.271163
H	9.112090	5.180929	0.848808	H	5.155714	-1.419623	-0.433354
H	7.560740	5.015143	1.695218	H	5.644042	-2.384420	0.965882
C	8.554516	3.567202	-1.321326	H	4.115331	-1.545782	0.993956
H	8.930789	2.620000	-0.921105	H	7.614573	-1.564012	1.476621
H	8.088096	3.358396	-2.290936	H	7.703907	-0.541199	0.034747
H	9.417178	4.222661	-1.492756	H	8.059582	0.126107	1.643912

Table S9: XYZ coordinates of the optimized S_0 structure for **(2)**

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

Table S10: XYZ coordinates of the optimized T_1 structure for **(2)**

Ir	-0.246975	-1.969450	-0.167601	H	9.174361 5.250536 0.861834
F	-2.140374	-2.769415	4.883679	C	-3.109551 -2.576307 -0.537876
F	-2.962253	-6.691073	-0.406279	C	-1.813594 -3.244660 -0.346843
O	1.167755	-3.482934	-0.066463	C	-1.795951 -4.626983 -0.316997
O	2.553127	-4.790518	-1.267128	H	-0.872326 -5.176172 -0.164245
O	2.681889	0.279000	1.799188	C	-2.998472 -5.341151 -0.450155
O	-3.882701	-0.175251	-0.618210	C	-4.248411 -4.716959 -0.608943
N	0.249464	-2.293317	-2.288028	H	-5.137036 -5.334666 -0.692921
N	1.428231	-0.598805	0.242000	C	-4.318905 -3.339750 -0.651618
N	2.495569	-0.002750	-0.396417	H	-5.272035 -2.834375 -0.771510
N	-1.685562	-0.642536	-0.439212	C	-3.768849 2.257678 -0.291376
N	-1.823349	0.689266	-0.270307	C	-3.341430 3.334023 -1.111471
C	1.699787	-3.919590	-1.177026	C	-4.846448 2.429310 0.620153
C	1.181888	-3.252585	-2.441543	C	-4.007840 4.557859 -0.994813
C	1.658297	-3.614890	-3.699173	C	-5.483626 3.669548 0.668948
H	2.410574	-4.393551	-3.752236	C	-5.082752 4.749883 -0.124982
C	1.151288	-2.968066	-4.823130	H	-3.687935 5.391246 -1.614834
H	1.501740	-3.231405	-5.817036	H	-6.310431 3.802878 1.360742
C	0.184874	-1.973765	-4.653504	C	-2.196849 3.210696 -2.115416
H	-0.236475	-1.444325	-5.501777	C	-0.925706 3.900176 -1.581725
C	-0.240816	-1.662568	-3.365553	C	-2.572761 3.741322 -3.512254
H	-0.984525	-0.896473	-3.173766	H	-1.093463 4.972566 -1.423383
C	1.569809	-0.432304	1.533391	H	-0.615172 3.456340 -0.630870
C	3.228000	0.513805	0.544565	H	-0.102113 3.788490 -2.297566
C	-2.967893	-1.210144	-0.602511	H	-1.761675 3.534350 -4.220429
C	-3.103500	0.955210	-0.380965	H	-3.483965 3.263978 -3.889647
C	0.642148	-1.003755	2.474163	H	-2.736151 4.824938 -3.514312
C	-0.367406	-1.804211	1.859301	C	-5.789995 6.096038 -0.049145
C	-1.304849	-2.397474	2.712373	C	-7.263365 5.990814 -0.487991
H	-2.092853	-3.035592	2.328724	C	-5.673105 6.729187 1.350799
C	-1.221859	-2.188201	4.085973	H	-7.834556 5.341536 0.186122
C	-0.232308	-1.407546	4.683431	H	-7.738502 6.979011 -0.480180
H	-0.216812	-1.287761	5.761104	H	-7.347541 5.578743 -1.499472
C	0.713074	-0.808383	3.859338	H	-6.133127 7.724365 1.361332
H	1.501474	-0.194774	4.285788	H	-6.180680 6.120566 2.108477
C	3.283426	3.132900	-0.843063	H	-4.625402 6.833858 1.653098
C	3.275679	2.901125	-2.367727	C	-5.308703 1.323184 1.569841
H	2.370889	3.329768	-2.815723	C	-5.372065 1.800676 3.033838
H	4.144409	3.373953	-2.842167	C	-6.659599 0.733166 1.119465
H	3.297856	1.831697	-2.598659	H	-6.148030 2.558894 3.188684
C	3.125405	4.627030	-0.506640	H	-5.605155 0.955126 3.691247
H	3.162956	4.800864	0.574467	H	-4.415454 2.226916 3.355060

H	3.903838	5.241043	-0.973846	H	-6.966243 -0.078338 1.790103
H	2.159708	4.990978	-0.875589	H	-7.447989 1.495646 1.131959
C	4.495853	1.257341	0.446084	H	-6.592558 0.330927 0.103739
C	4.527671	2.510116	-0.213554	C	5.673981 -0.666858 1.695281
C	5.752702	3.176152	-0.301125	C	6.766662 -1.602754 1.144627
H	5.789767	4.134587	-0.810378	C	5.795652 -0.506600 3.223741
C	6.927989	2.655275	0.250974	H	6.681560 -1.716418 0.058767
C	6.859819	1.419317	0.897447	H	7.774653 -1.235919 1.369497
H	7.769046	1.003273	1.323594	H	6.669104 -2.595888 1.597106
C	5.668434	0.694386	1.001149	H	4.981664 0.108294 3.621985
C	8.249529	3.406110	0.152825	H	5.757879 -1.485431 3.715882
C	8.695175	3.594452	-1.309923	H	6.744125 -0.028151 3.496053
H	7.989052	4.223012	-1.865405	H	-1.956750 2.150473 -2.229948
H	9.676925	4.080831	-1.351990	H	-5.283011 6.766523 -0.756325
H	8.767127	2.632856	-1.829551	H	-4.575921 0.512643 1.540140
C	8.196516	4.755697	0.894539	H	2.404447 2.621446 -0.438280
H	7.465114	5.433204	0.438319	H	9.008658 2.787381 0.650197
H	7.916955	4.620747	1.945123	H	4.717439 -1.160441 1.495020

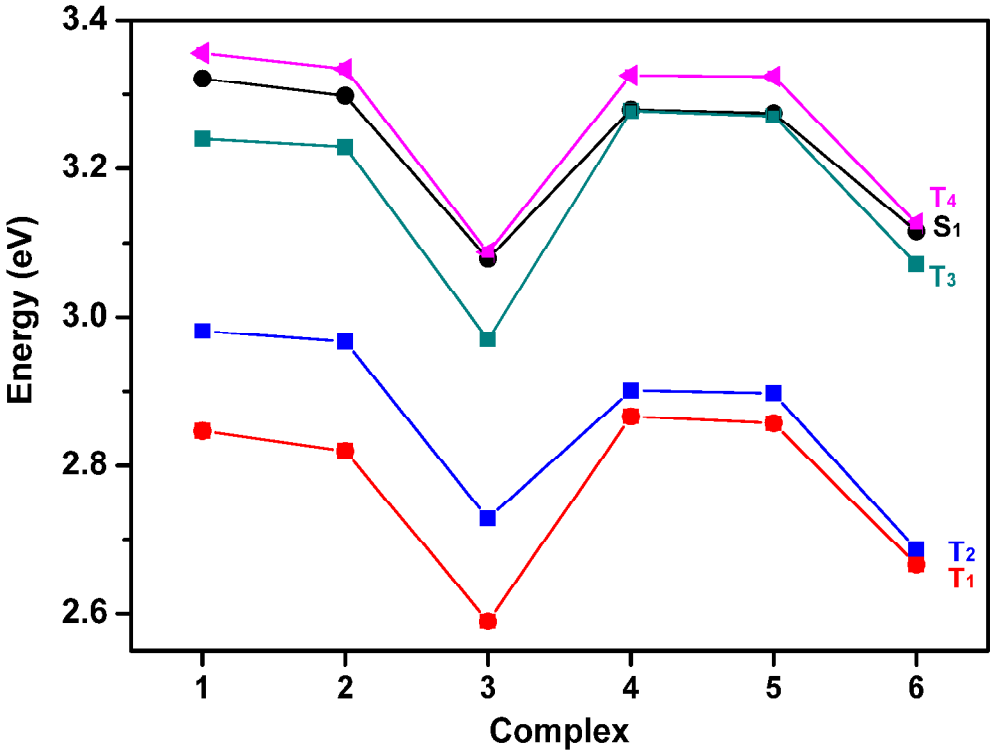

Figure S1. The excited states energy ordering in complexes **1**-**6.**

Complete author list of reference 24

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