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Electronic Supplementary Information

Theoretical study on supramolecularly-caged positively charged iridium (III) 2-pyridyl azolate derivatives as blue emitters for light-emitting electrochemical cells

Xiaochun Qu [a,b], Yuqi Liu [b], Yanling Si [b,c], Xue Wu [a,*] and Zhijian Wu [b,*]

[a] Department of Chemistry, College of Science, Yanbian University, Yanji, 133002, PR China.

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

[c] College of Resource and Environmental Science, Jilin Agricultural University, Changchun 130118, PR China

Table S1 Selected bond distances (Å), bond angles (°) and dihedral angles (°) for **1a** in ground-state at B3LYP, CAM-B3LYP, PBE0, B3PW91 and O3LYP level of theory, respectively, along with the experimental data

	B3LYP	**CAM-B3LYP**	**PEB0**	**B3PW91**	**O3LYP**	**Exp.**[a]
			Bond Length			
Ir-N1	2.083	2.072	2.058	2.064	2.067	2.050
Ir-C2	2.014	2.008	1.998	2.003	1.996	2.000
Ir-N3	2.082	2.073	2.054	2.062	2.066	2.052
Ir-C4	2.024	2.017	2.007	2.013	2.010	2.015
Ir-N5	2.285	2.245	2.224	2.244	2.300	2.174
Ir-N6	2.247	2.221	2.201	2.213	2.243	2.179
N7-C8	1.436	1.433	1.427	1.430	1.436	1.432
			Bond Angle			
N1-Ir-N3	173.27	172.86	172.75	172.99	174.83	172.66
N2-Ir-N5	167.43	168.08	167.96	167.90	168.92	167.21
C4-Ir-N6	175.92	175.88	176.36	176.58	177.11	177.89
N1-Ir-C2	80.24	80.32	80.521	80.41	80.35	80.78
N3-Ir-C4	80.03	80.10	80.28	80.18	80.15	80.04
N5-Ir-N6	73.53	74.09	74.36	74.14	73.39	74.61
N5-N7-C8	124.06	123.67	123.63	124.07	124.98	123.02
			Dihedral Angle			
ω2	-64.97	-66.66	-61.33	-62.971	-113.81	-51.92

ω2= N5-N7-C8-C9

[a] Ref. 27

Table S2 Selected bond distances (Å), bond angles (°) and dihedral angles (°) for **7a** and **7b** in ground-state at PBE0 level of theory, respectively, along with the experimental data

	7a		**7b**	
	Cal.	Exp.[a]	Cal.	Exp.[a]
		Bond Length		
Ir-N1	2.058	2.046	2.056	2.030
Ir-C2	2.002	2.004	1.998	2.006
Ir-N3	2.057	2.047	2.056	2.032
Ir-C4	2.002	2.011	2.000	1.992
Ir-N5	2.162	2.126	2.155	2.124
Ir-N6	2.199	2.136	2.193	2.136
		Bond Angle		
N1-Ir-N3	173.45	172.79	173.51	174.27
N2-Ir-N5	172.17	174.62	172.51	173.61
C4-Ir-N6	171.8	171.01	172.3	172.49
N1-Ir-C2	80.40	80.65	80.54	80.19
N3-Ir-C4	80.41	80.20	80.48	79.82
N5-Ir-N6	74.29	75.45	74.48	75.28

[a] Ref. 30

Table S3 Calculated intramolecular centroid-centroid distances (Å) for **1a**-**6a** and **1b**-**6b** at DFT/PBE0 level of theory

	1a	**2a**	**3a**	**4a**	**5a**	**6a**
R(S_0)	3.890	4.181	4.126	4.158	4.135	3.927
R(T_1)	3.847	3.852	3.827	3.979	4.138	3.784
	1b	**2b**	**3b**	**4b**	**5b**	**6b**
R(S_0)	3.795	4.061	3.969	4.038	3.977	3.882
R(T_1)	3.784	4.288	4.202	3.898	3.773	3.831

Table S4 Selected bond distances (Å), bond angles (°) and dihedral angles (°) for **1a-7a** and **1b-7b** in T_1 states at DFT/PBE0 level of theory

	1a	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**
				Bond Length			
Ir-N1	2.068	2.057	2.057	2.058	2.067	2.053	2.057
Ir-C2	1.995	1.991	1.994	1.992	1.992	1.991	1.985
Ir-N3	2.034	2.052	2.052	2.051	2.036	2.051	2.048
Ir-C4	1.968	1.972	1.973	1.965	1.968	1.970	1.964
Ir-N5	2.249	2.175	2.171	2.203	2.273	2.215	2.178
Ir-N6	2.221	2.184	2.182	2.207	2.231	2.190	2.178
X7-C8	1.427	1.465	1.464	1.402	1.425	1.403	-
				Bond Angle			
N1-Ir-N3	173.90	175.77	175.73	175.47	174.10	178.22	176.37
C2-Ir-N5	167.53	165.36	164.85	174.17	167.09	168.83	170.69
C4-Ir-N6	176.19	174.30	174.10	164.46	176.05	174.00	164.05
				Dihedral Angle			
Φ1	-1.37	0.92	0.94	0.56	-1.32	0.68	-0.40
Φ2	0.15	2.20	1.91	0.48	-0.33	2.47	0.16
ω1	-2.77	-3.24	-11.86	-12.13	-0.98	14.84	15.86
ω2	-60.43	-50.29	-47.71	-20.84	-54.07	19.69	-

	1b	**2b**	**3b**	**4b**	**5b**	**6b**	**7b**
				Bond Length			
Ir-N1	2.065	2.058	2.060	2.059	2.053	2.051	2.047
Ir-C2	1.992	1.997	1.999	1.996	1.997	1.995	1.965
Ir-N3	2.028	2.052	2.050	2.051	2.048	2.050	2.054
Ir-C4	1.985	2.004	2.002	1.971	1.983	1.975	1.991
Ir-N5	2.230	2.231	2.215	2.201	2.163	2.196	2.180
Ir-N6	2.201	2.171	2.170	2.192	2.175	2.177	2.169
X7-C8	1.428	1.450	1.449	1.387	1.404	1.400	-
				Bond Angle			
N1-Ir-N3	173.75	173.01	173.09	174.37	176.90	177.68	176.32
C2-Ir-N5	169.09	168.91	168.79	166.07	169.92	170.09	172.21
C4-Ir-N6	176.56	176.83	177.43	174.45	175.98	174.45	162.85
				Dihedral Angle			
Φ1	-1.13	-1.15	-1.07	-0.09	0.64	0.463	0.10
Φ2	-0.83	0.11	0.29	-0.95	-0.39	1.19	0.99
ω1	-2.07	-0.50	7.80	-11.32	8.89	13.95	-17.83
ω2	-64.56	-34.75	-36.49	-17.89	29.28	20.95	-

X=N (in **1a**/**1b** and **4a-7a**/**4b-7b**); X=C (in **2a-3a**/**2b-3b**)

Φ1=N1-C_{ppy1}-C'$_{ppy1}$-C2; Φ2=N3-C_{ppy2}-C'$_{ppy2}$-C4; ω1=N5-C_{phazpy}-C'$_{phazpy}$-N6; ω2= N5-X7-C8-C9

Table S5 Variations for bond distances (Å), bond angles (°) and dihedral angles (°) upon $S_0 \rightarrow T_1$ transition for **1a-7a** and **1b-7b**

	1a	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**
				Bond Length			
Ir-N1	0.010	0.001	0.002	0.001	0.011	-0.003	-0.001
Ir-C2	-0.003	-0.007	-0.006	-0.003	-0.003	-0.003	-0.017
Ir-N3	-0.020	-0.002	-0.003	-0.006	-0.021	-0.006	-0.009
Ir-C4	-0.038	-0.033	-0.034	-0.042	-0.038	-0.037	-0.037
Ir-N5	0.025	-0.069	-0.055	-0.048	0.036	-0.021	0.016
Ir-N6	0.019	-0.021	-0.015	-0.001	0.020	-0.019	-0.021
X7-C8	-0.000	-0.002	-0.004	-0.023	-0.001	-0.032	-
				Bond Angle			
N1-Ir-N3	1.14	2.96	3.02	2.54	1.08	4.17	2.92
C2-Ir-N5	-0.42	-2.75	-3.37	-2.90	-0.97	-0.78	-1.47
C4-Ir-N6	-0.16	-2.29	-1.97	-2.42	-0.30	-3.68	-7.75
				Dihedral Angle			
Φ1	0.21	2.80	2.93	2.05	0.13	1.89	-1.95
Φ2	-0.16	1.72	1.45	0.39	-0.21	2.05	-1.31
ω1	-0.13	-1.00	-8.66	-7.76	-0.39	7.79	19.59
ω2	0.90	-1.03	5.04	25.68	2.76	-32.18	-

	1b	**2b**	**3b**	**4b**	**5b**	**6b**	**7b**
				Bond Length			
Ir-N1	0.008	0.000	0.003	-0.000	-0.005	-0.004	-0.008
Ir-C2	-0.003	0.001	0.001	0.004	0.003	0.003	-0.033
Ir-N3	-0.026	0.000	-0.002	-0.003	-0.007	-0.007	-0.002
Ir-C4	-0.019	0.003	-0.000	-0.032	-0.019	-0.029	-0.009
Ir-N5	0.024	0.008	0.009	-0.028	-0.047	-0.023	0.025
Ir-N6	0.007	-0.029	-0.022	-0.010	-0.032	-0.024	-0.024
X7-C8	-0.001	-0.018	-0.019	-0.039	-0.023	-0.036	-
				Bond Angle			
N1-Ir-N3	0.88	0.30	0.37	1.64	4.01	3.41	2.82
C2-Ir-N5	-0.11	-0.25	-0.34	-2.20	0.72	-0.30	-0.30
C4-Ir-N6	0.00	-0.14	0.77	-2.62	-0.44	-2.94	-9.44
				Dihedral Angle			
Φ1	0.06	0.59	0.53	1.48	1.79	1.28	1.44
Φ2	-1.27	-0.28	-0.03	-0.89	-0.30	0.83	2.34
ω1	-0.69	1.24	10.62	-7.63	9.16	6.89	-21.90
ω2	3.32	19.30	20.09	33.00	92.50	-34.33	-

X=N (in **1a**/**1b** and **4a-7a**/**4b-7b**); X=C (in **2a-3a**/**2b-3b**)

Φ1=N1-C_{ppy1}-C'$_{ppy1}$-C2; Φ2=N3-C_{ppy2}-C'$_{ppy2}$-C4; ω1=N5-C_{phazpy}-C'$_{phazpy}$-N6; ω2= N5-X7-C8-C9

Table S6 Selected bond distances (Å) and bond angles (°) for **1a-7a** and **1b-7b** in the metal-centered (^{3}MC) triplet excited states at DFT/PBE0 level of theory

	1a	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**
				Bond Length			
Ir-N1	2.395	2.411	2.423	2.411	2.405	2.446	2.450
Ir-C2	2.024	1.997	2.023	1.988	1.988	1.994	1.985
Ir-N3	2.155	2.454	2.178	2.435	2.438	2.443	2.468
Ir-C4	2.013	1.976	2.013	1.980	1.985	1.993	1.986
Ir-N5	2.566	2.226	2.482	2.269	2.252	2.247	2.177
Ir-N6	2.232	2.254	2.234	2.247	2.251	2.232	2.219
X7-C8	1.423	1.467	1.466	1.423	1.425	1.433	173.76
				Bond Angle			
N1-Ir-N3	147.37	172.71	146.28	173.92	174.38	176.42	167.47
C2-Ir-N5	174.89	175.06	172.99	175.65	175.37	176.24	169.70
C4-Ir-N6	143.69	161.32	141.84	162.13	164.07	167.85	-
				Dihedral Angle			
Φ1	0.34	-11.84	1.45	-10.54	-10.78	-8.44	4.82
Φ2	-7.85	-17.07	-6.88	-17.45	-17.24	2.74	11.59
ω1	9.39	-5.23	5.274	-7.32	-2.17	5.91	-1.79
ω2	-40.58	-50.30	-24.38	-42.35	-57.36	47.13	-
	1b	**2b**	**3b**	**4b**	**5b**	**6b**	**7b**
				Bond Length			
Ir-N1	2.481	2.474	2.426	2.226	2.361	2.414	2.435
Ir-C2	2.015	2.018	2.025	2.004	2.028	2.006	2.001
Ir-N3	2.199	2.183	2.165	2.546	2.128	2.423	2.421
Ir-C4	2.014	2.012	2.012	2.014	2.011	2.008	1.999
Ir-N5	2.331	2.362	2.443	2.230	2.610	2.228	2.164
Ir-N6	2.199	2.214	2.220	2.259	2.232	2.215	2.213
X7-C8	1.427	1.466	1.466	1.426	1.422	1.434	173.88
				Bond Angle			
N1-Ir-N3	156.82	150.45	148.67	160.35	146.08	176.46	170.65
C2-Ir-N5	177.04	178.52	173.85	167.20	176.04	175.86	171.91
C4-Ir-N6	147.74	147.04	142.99	149.87	143.97	170.10	-
				Dihedral Angle			
Φ1	0.79	-0.48	1.80	-7.06	-0.04	-8.48	-10.27
Φ2	-8.75	-4.77	-6.42	-0.73	-6.96	0.16	-4.255
ω1	-2.80	7.36	5.19	-4.96	6.64	5.36	1.0684
ω2	-57.28	34.57	-32.14	-49.20	-35.30	50.88	-

X=N (in **1a**/**1b** and **4a-7a**/**4b-7b**); X=C (in **2a-3a**/**2b-3b**)

Φ1=N1-C_{ppy1}-C'_{ppy1}-C2; Φ2=N3-C_{ppy2}-C'_{ppy2}-C4; ω1=N5-C_{phazpy}-C'_{phazpy}-N6; ω2= N5-X7-C8-C9

Table S7 Molecular orbital composition (%) and energy levels of **1a-7a** in ground the state

	MO	Energy	Contribution				
		(eV)	phazpy	Ir	ppy2	ppy1	
1a	L+3	-3.66	87	1	4	9	π*(phazpy)
	L+2	-3.74	3	5	55	37	π*(ppy)
	L+1	-3.88	3	4	39	54	π*(ppy)
	L	-4.38	96	3	1	1	π*(phazpy)
	H	-8.05	2	33	41	23	5d+ π(ppy)
	H-1	-8.58	3	5	44	48	π(ppy)
	H-2	-8.78	3	23	53	21	5d+π(ppy)
	H-3	-8.94	6	21	12	61	5d+π(ppy)
2a	L+3	-3.68	1	5	66	29	π*(ppy)
	L+2	-3.82	4	4	28	64	π*(ppy)
	L+1	-3.92	93	1	1	4	π*(phazpy)
	L	-4.63	97	3	0	1	π*(phazpy)
	H	-7.95	3	33	44	20	5d+ π(ppy)
	H-1	-8.52	6	6	41	47	π(ppy)
	H-2	-8.70	6	19	60	15	5d+π(ppy)
	H-3	-8.90	15	13	5	67	5d+π(ppy)+π(phazpy)
3a	L+3	-3.58	2	5	64	29	π*(ppy)
	L+2	-3.67	85	1	8	6	π*(phazpy)
	L+1	-3.72	9	4	24	63	π*(ppy)
	L	-4.41	96	3	0	1	π*(phazpy)
	H	-7.84	3	34	44	20	5d+ π(ppy)
	H-1	-8.40	7	6	38	48	π(ppy)
	H-2	-8.58	8	22	57	13	5d+π(ppy)
	H-3	-8.78	17	16	4	63	5d+π(ppy)+ π(phazpy)
4a	L+3	-3.85	86	1	2	11	π*(phazpy)
	L+2	-3.90	7	5	52	36	π*(ppy)
	L+1	-4.01	5	5	40	50	π*(ppy)
	L	-4.66	95	3	1	1	π*(phazpy)
	H	-8.21	2	33	42	23	5d+ π(ppy)
	H-1	-8.73	3	5	44	48	π(ppy)
	H-2	-8.93	2	16	61	22	5d+π(ppy)
	H-3	-9.10	3	12	20	65	5d+π(ppy)
5a	L+3	-3.72	85	1	5	9	π*(phazpy)
	L+2	-3.85	3	5	44	48	π*(ppy)
	L+1	-3.98	2	5	49	44	π*(ppy)
	L	-4.54	96	3	1	1	π*(phazpy)

	H	-8.16	2	34	39	26	5d+ π(ppy)
	H-1	-8.71	2	5	45	48	π(ppy)
	H-2	-8.91	2	19	53	26	5d+π(ppy)
	H-3	-9.05	4	15	22	59	5d+π(ppy)
6a	L+3	-3.84	56	2	26	16	π*(phazpy)+π*(ppy)
	L+2	-3.93	34	4	58	4	π*(phazpy)+π*(ppy)
	L+1	-4.04	3	5	11	81	π*(ppy)
	L	-4.66	96	3	0	1	π*(phazpy)
	H	-8.23	2	34	39	25	5d+ π(ppy)
	H-1	-8.79	2	3	43	52	π(ppy)
	H-2	-8.99	1	13	63	23	5d+π(ppy)
	H-3	-9.10	4	16	23	58	5d+π(ppy)
7a	L+3	-3.84	2	4	25	69	π*(ppy)
	L+2	-3.92	1	5	69	25	π*(ppy)
	L+1	-4.15	96	1	2	1	π*(azpy)
	L	-4.61	96	3	0	1	π*(azpy)
	H	-8.11	2	33	30	36	5d+ π(ppy)
	H-1	-8.72	1	4	46	49	π(ppy)
	H-2	-8.91	1	12	34	54	5d+π(ppy)
	H-3	-9.02	3	13	57	28	5d+π(ppy)

Table S8 Molecular orbital composition (%) and energy levels of **1b**-**7b** in ground the state

	MO	Energy (eV)	Contribution phazpy	Ir	dfppy2	dfppy1	
1b	L+3	-3.85	87	1	5	8	π*(phazpy)
	L+2	-3.91	7	5	52	36	π*(ppy)
	L+1	-4.04	2	5	39	54	π*(ppy)
	L	-4.58	96	3	0	1	π*(phazpy)
	H	-8.46	2	31	43	24	5d+π(ppy)
	H-1	-8.79	2	5	64	29	π(ppy)
	H-2	-8.89	1	8	30	61	π(ppy)
	H-3	-9.20	7	11	30	53	π(ppy)
2b	L+3	-3.85	1	5	68	26	π*(ppy)
	L+2	-3.98	2	4	26	68	π*(ppy)
	L+1	-4.11	96	1	1	2	π*(phazpy)
	L	-4.83	97	3	0	0	π*(phazpy)
	H	-8.35	3	31	46	20	5d+π(ppy)
	H-1	-8.70	2	6	71	21	π(ppy)
	H-2	-8.83	5	7	25	63	π(ppy)
	H-3	-9.08	48	7	6	38	π(phazpy)+π(ppy)

3b	L+3	-3.74	2	5	69	25	π*(ppy)
	L+2	-3.86	85	1	7	7	π*(phazpy)
	L+1	-3.88	10	4	20	65	π*(ppy)
	L	-4.60	96	3	0	1	π*(phazpy)
	H	-8.23	4	31	46	19	5d+ π(ppy)
	H-1	-8.59	3	7	71	20	π(ppy)
	H-2	-8.72	6	8	25	61	π(ppy)
	H-3	-8.94	50	8	5	38	π(phazpy)+π(ppy)
4b	L+3	-4.04	65	2	12	21	π*(phazpy)+π*(ppy)
	L+2	-4.06	30	4	41	24	π*(phazpy)+π*(ppy)
	L+1	-4.18	3	5	41	51	π*(ppy)
	L	-4.85	96	3	1	1	π*(phazpy)
	H	-8.61	2	29	45	24	5d+π(ppy)
	H-1	-8.92	2	5	65	28	π(ppy)
	H-2	-9.04	1	7	30	61	π(ppy)
	H-3	-9.35	7	4	31	57	π(ppy)
5b	L+3	-3.91	89	1	4	6	π*(phazpy)
	L+2	-4.02	4	5	45	46	π*(ppy)
	L+1	-4.14	1	5	48	46	π*(ppy)
	L	-4.74	96	3	0	1	π*(phazpy)
	H	-8.56	2	31	40	27	5d+π(ppy)
	H-1	-8.90	1	4	60	35	π(ppy)
	H-2	-9.00	1	8	35	57	π(ppy)
	H-3	-9.32	5	6	36	53	π(ppy)
6b	L+3	-4.02	46	2	38	13	π*(phazpy)+π*(ppy)
	L+2	-4.11	48	3	46	3	π*(phazpy)+π*(ppy)
	L+1	-4.20	3	5	9	83	π*(ppy)
	L	-4.86	96	3	0	1	π*(phazpy)
	H	-8.63	2	30	43	25	5d+π(ppy)
	H-1	-9.00	1	4	58	38	π(ppy)
	H-2	-9.08	1	7	37	55	π(ppy)
	H-3	-9.35	5	5	36	54	π(ppy)
7b	L+3	-4.01	2	4	69	25	π*(ppy)
	L+2	-4.11	1	5	25	69	π*(ppy)
	L+1	-4.35	96	1	1	1	π*(azpy)
	L	-4.82	96	3	1	0	π*(azpy)
	H	-8.54	2	30	38	31	5d+π(ppy)
	H-1	-8.91	0	4	60	36	π(ppy)
	H-2	-9.00	0	6	35	58	π(ppy)
	H-3	-9.34	2	4	44	50	π(ppy)

Table S9 Calculated excited energies, dominant orbital excitations, and oscillator strength (*f*) from PCM-TD -B3LYP calculations in CH_3CN media for **1a-7a**

	State	E_{th} eV	λ_{cal} nm	λ_{exp} nm	*f*	Excitation (contribution)	Character
1a	S_1	2.97	417.3	411	0.0021	H→L (98%)	MLCT/LLCT
	S_2	3.15	393.5	385	0.0489	H→L+1 (96%)	MLCT/ILCT
	S_5	3.62	342.6		0.0421	H-1→L (84%)	LLCT
	S_9	3.84	322.9		0.0518	H-3→L (66%)	MLCT/ILCT/LLCT
	S_{13}	3.96	313.2		0.0389	H-3→L+1 (24%), H-2→L+2 (45%)	MLCT/ILCT
	S_{16}	4.15	298.8		0.0690	H-4→L+2 (10%), H-3→L+2 (55%)	MLCT/ILCT/LLCT
	S_{18}	4.23	293.4		0.0581	H-4→L+1 (61%), H-2→L+3 (13%)	MLCT/ILCT
	S_{20}	4.29	288.8		0.0624	H-6→L (27%), H-2→L+3 (48%)	MLCT/ILCT/LLCT
	S_{23}	4.36	284.3		0.0629	H-4→L+2 (32%), H-1→L+3 (13%)	MLCT/ILCT
	S_{24}	4.41	281.0		0.1674	H-6→L(27%), H-5→L+2(16%), H-1→L+3(16%)	MLCT/ILCT
	S_{25}	4.45	278.3		0.0564	H-5→L+2 (50%), H-1→L+5 (11%)	MLCT/ILCT
	S_{27}	4.52	274.1		0.0342	H-3→L+3 (64%)	MLCT/ILCT/LLCT
	S_{28}	4.53	273.6		0.0418	H-2→L+4 (32%), H-1→L+4 (28%)	MLCT/ILCT
	S_{29}	4.55	272.2		0.0376	H→L+7 (84%)	MLCT/ILCT/LLCT
	S_{30}	4.59	269.9		0.0678	H-6→L+1 (75%)	ILCT/LLCT
	S_{31}	4.63	267.6		0.1133	H-2→L+5 (38%), H-1→L+4 (15%)	MLCT/ILCT/LLCT
	S_{32}	4.66	265.9	256	0.3550	H-5→L+2 (12%), H-1→L+5 (40%)	MLCT/ILCT
	S_{37}	4.78	259.4		0.0428	H-6→L+2 (13%), H-3→L+5 (55%)	MLCT/ILCT/LLCT
	S_{39}	4.91	252.3		0.0448	H-4→L+4 (43%), H→L+8 (19%)	MLCT/ILCT
	S_{42}	4.95	250.7		0.0751	H-4→L+4 (23%), H→L+8 (20%)	MLCT/ILCT/LLCT
	S_{51}	5.12	242.1		0.1060	H-9→L (18%), H-8→L (27%), H-6→L+3 (19%)	MLCT/ILCT/LLCT
	S_{57}	5.22	237.4		0.0326	H-3→L+6 (12%), H-2→L+11 (29%)	ILCT/LLCT
	S_{58}	5.25	236.0		0.0726	H-6→L+4 (70%)	ILCT/LLCT
	T_1	2.76	448.9		0.0000	H-1→L+2 (16%), H→L+1 (55%)	MLCT/ILCT
	T_2	2.83	438.8		0.0000	H-1→L+1 (30%), H→L+2 (41%)	MLCT/ILCT
	T_3	2.95	420.3	411	0.0000	H→L (91%)	MLCT/LLCT
2a	S_1	2.82	439.5		0.0019	H→L (98%)	MLCT/LLCT
	S_2	3.12	398.0		0.0498	H→L+1 (97%)	MLCT/LLCT
	S_5	3.50	354.5		0.0392	H-1→L (83%)	LLCT
	S_7	3.73	332.6		0.0660	H-4→L (71%), H-3→L (10%)	MLCT/ILCT/LLCT
	S_{11}	3.83	323.4		0.1663	H-4→L (11%), H-3→L (69%), H-2→L (10%)	MLCT/ILCT/LLCT
	S_{13}	3.90	318.1		0.0407	H-1→L+2 (69%)	MLCT/ILCT
	S_{14}	3.94	314.7		0.0772	H-5→L (14%), H-2→L+2 (44%)	MLCT/ILCT
	S_{18}	4.14	299.4		0.0609	H-4→L+1 (13%), H-4→L+2 (46%)	MLCT/ILCT/LLCT
	S_{19}	4.15	298.8		0.0396	H-4→L+1 (11%), H-3→L+1 (57%)	MLCT/ILCT/LLCT
	S_{20}	4.19	295.6		0.0328	H-2→L+3(36%), H-1→L+3 (20%)	MLCT/ILCT
	S_{22}	4.26	291.0		0.1250	H-5→L+1 (58%)	MLCT/ILCT

	S_{24}	4.33	286.6	0.0344	H-6→L+1 (17%), H-5→L+2(29%), H-1→L+4 (21%)	MLCT/ILCT
	S_{29}	4.44	279.1	0.0312	H-6→L+2 (34%), H-2→L+4 (29%)	MLCT/ILCT
	S_{33}	4.62	268.5	0.1567	H-1→L+4 (24%), H-1→L+5 (31%)	MLCT/ILCT
	S_{34}	4.64	267.3	0.2957	H-2→L+5 (26%), H-1→L+5 (12%)	MLCT/ILCT
	S_{36}	4.70	263.7	0.0377	H-4→L+4 (54%), H-3→L+4 (11%)	MLCT/ILCT/LLCT
	S_{39}	4.77	260.0	0.0353	H-7→L+1 (13%), H-4→L+5 (43%)	MLCT/ILCT/LLCT
	S_{40}	4.78	259.5	0.0489	H-8→L (33%), H-4→L+4 (10%), H→L+7 (28%)	MLCT/ILCT/LLCT
	S_{42}	4.79	258.7	0.1689	H-3→L+4 (20%), H→L+7 (41%)	MLCT/ILCT
	S_{47}	4.94	250.8	0.2106	H-5→L+4 (12%), H→L+8 (45%)	MLCT/ILCT/LLCT
	T_1	2.74	452.4	0.0000	H-1→L+2 (11%), H→L (18%), H→L+1 (49%)	MLCT/ILCT/LLCT
	T_2	2.80	442.8	0.0000	H→L (51%), H→L+2 (23%)	MLCT/ILCT/LLCT
	T_3	2.82	440.3	0.0000	H-1→L+1 (16%), H→L (28%),H→L+2 (24%)	MLCT/ILCT/LLCT
3a	S_1	2.82	439.5	0.0023	H→L (98%)	MLCT/LLCT
	S_2	3.12	397.2	0.0476	H→L+1 (97%)	MLCT/ILCT
	S_5	3.49	355.1	0.0498	H-1→L (86%)	LLCT
	S_7	3.71	333.9	0.0777	H-4→L (66%), H-3→L (16%)	MLCT/ILCT/LLCT
	S_{11}	3.84	322.6	0.1422	H-4→L (16%), H-3→L (65%)	MLCT/ILCT/LLCT
	S_{13}	3.90	318.2	0.0386	H-1→L+2 (67%)	MLCT/ILCT/LLCT
	S_{14}	3.94	314.9	0.0774	H-4→L+1 (10%), H-2→L+2 (49%)	MLCT/ILCT/LLCT
	S_{18}	4.13	300.2	0.0722	H-4→L+2 (49%), H-3→L+2 (14%)	MLCT/ILCT/LLCT
	S_{22}	4.26	290.7	0.1245	H-5→L+1 (56%), H-2→L+3 (15%)	MLCT/ILCT
	S_{34}	4.62	268.6	0.1330	H-1→L+4 (26%), H-1→L+5 (24%)	MLCT/ILCT/LLCT
	S_{35}	4.63	267.5	0.3014	H-2→L+5 (23%), H-1→L+5 (18%)	MLCT/ILCT/LLCT
	S_{36}	4.64	267.0	0.0487	H-10→L (24%), H-8→L (47%), H→L+8 (13%)	ILCT/LLCT
	S_{39}	4.70	263.6	0.0336	H-4→L+4 (44%), H-3→L+4 (15%)	MLCT/ILCT
	S_{42}	4.76	260.6	0.0459	H-10→L (34%), H-8→L (14%), H-6→L+3 (16%)	MLCT/ILCT
	S_{45}	4.79	259.0	0.0490	H-6→L+3 (48%), H→L+9 (32%)	MLCT/ILCT
	S_{46}	4.80	258.2	0.0692	H-4→L+4 (20%), H-3→L+4 (52%)	MLCT/ILCT
	S_{52}	4.95	250.3	0.1438	H-1→L+6 (14%), H→L+10 (35%)	MLCT/ILCT/LLCT
	S_{53}	4.96	250.0	0.0443	H-2→L+6 (19%), H-1→L+6 (24%) H→L+10 (18%)	MLCT/ILCT
	S_{56}	5.00	247.8	0.0776	H-2→L+7 (24%), H-1→L+7 (15%)	MLCT/ILCT/LLCT
	T_1	2.74	452.2	0.0000	H-1→L+2 (11%), H→L (25%), H→L+1 (44%)	MLCT/ILCT/LLCT
	T_2	2.80	442.4	0.0000	H→L (48%), H→L+2 (24%)	MLCT/ILCT/LLCT
	T_3	2.82	440.0	0.0000	H→L (24%), H→L+1 (16%), H→L+2 (23%)	MLCT/ILCT/LLCT
4a	S_1	2.80	443.2	0.0027	H→L (99%)	MLCT/LLCT
	S_2	3.19	388.8	0.0511	H→L+1 (97%)	MLCT/ILCT
	S_6	3.70	335.0	0.0524	H-3→L (49%), H→L+3 (38%)	MLCT/LLCT
	S_{11}	3.88	319.9	0.0432	H-2→L+1 (54%), H-1→L+1 (16%)	MLCT/ILCT
	S_{17}	4.15	299.0	0.1609	H-6→L (50%), H-3→L+1 (23%)	MLCT/ILCT
	S_{18}	4.16	298.3	0.1441	H-6→L (38%), H-3→L+1 (27%)	MLCT/ILCT
	S_{19}	4.18	296.5	0.0827	H-3→L+2 (68%)	MLCT/ILCT/LLCT
	S_{20}	4.25	291.8	0.0791	H-4→L+1 (59%)	MLCT/ILCT

	S_{21}	4.27	290.4	0.0671	H-5→L+1(16%), H-4→L+2(15%), H-1→L+3 (31%),	MLCT/ILCT
	S_{23}	4.36	284.1	0.0502	H-5→L+1 (17%), H-1→L+3 (46%)	MLCT/ILCT/LLCT
	S_{24}	4.39	282.2	0.0463	H-5→L+2 (15%), H-2→L+3 (47%)	MLCT/ILCT/LLCT
	S_{25}	4.44	279.0	0.0532	H-5→L+2 (42%), H-2→L+3 (21%)	MLCT/ILCT
	S_{27}	4.52	274.5	0.0719	H-1→L+4 (53%)	MLCT/ILCT
	S_{30}	4.61	269.1	0.0487	H-6→L+1 (62%), H→L+7 (16%)	MLCT/ILCT/LLCT
	S_{31}	4.62	268.6	0.0438	H-6→L+1 (23%), H→L+7 (62%)	MLCT/ILCT/LLCT
	S_{33}	4.69	264.5	0.2699	H-1→L+5 (45%), H→L+7 (12%)	MLCT/ILCT/LLCT
	S_{37}	4.75	260.8	0.0648	H-6→L+2 (37%), H-2→L+6 (15%)	MLCT/ILCT/LLCT
	S_{38}	4.78	259.1	0.0364	H-9→L (45%), H-8→L (22%), H-2→L+6 (13%)	MLCT/LLCT
	S_{39}	4.80	258.1	0.0565	H-9→L (17%), H-2→L+6 (39%)	MLCT/ILCT/LLCT
	S_{43}	4.90	253.1	0.1261	H→L+8 (31%), H→L+10 (14%)	MLCT/ILCT/LLCT
	S_{44}	4.95	250.6	0.0524	H-3→L+6 (32%), H→L+9 (12%)	MLCT/ILCT/LLCT
	S_{46}	4.98	249.0	0.0319	H-7→L+1 (43%), H-5→L+4 (14%)	MLCT/ILCT/LLCT
	S_{49}	5.00	247.8	0.0514	H-8→L (13%), H-6→L+3 (15%), H→L+8 (28%)	MLCT/ILCT/LLCT
	S_{51}	5.07	244.4	0.0827	H-6→L+3 (42%), H-4→L+6 (28%)	MLCT/ILCT
	S_{53}	5.10	243.3	0.0800	H-5→L+5 (36%), H-4→L+6 (26%)	MLCT/ILCT
	T_1	2.74	453.2	0.0000	H→L (61%), H→L+1 (19%)	MLCT/ILCT/LLCT
	T_2	2.81	440.7	0.0000	H→L (36%), H→L+1 (35%)	MLCT/ILCT/LLCT
	T_3	2.83	437.8	0.0000	H-1→L+1 (28%), H→L+2 (37%)	MLCT/ILCT
5a	S_1	2.84	436.4	0.0014	H→L (99%)	MLCT/LLCT
	S_2	3.17	391.0	0.0517	H→L+1 (97%)	MLCT/ILCT
	S_7	3.75	330.9	0.0843	H-3→L (73%)	MLCT/LLCT
	S_8	3.84	323.1	0.0335	H-2→L+1 (70%)	MLCT/ILCT
	S_{17}	4.17	297.2	0.0593	H-3→L+2 (49%), H→L+6 (12%)	MLCT/ILCT
	S_{19}	4.25	291.9	0.0806	H-4→L+1 (59%), H-2→L+3 (10%)	MLCT/ILCT
	S_{20}	4.26	290.9	0.0341	H-5→L+1 (15%), H-1→L+3 (43%)	MLCT/ILCT/LLCT
	S_{21}	4.34	286.0	0.0571	H-6→L (29%), H-2→L+3 (42%)	MLCT/ILCT/LLCT
	S_{23}	4.38	283.1	0.0416	H-4→L+2 (17%), H-1→L+3 (35%)	MLCT/ILCT/LLCT
	S_{24}	4.42	280.7	0.1390	H-6→L (38%), H-5→L+2 (25%)	MLCT/ILCT
	S_{25}	4.45	278.3	0.1135	H-6→L (13%), H-5→L+2 (43%), H-2→L+3 (13%)	MLCT/ILCT
	S_{26}	4.54	272.9	0.0433	H-3→L+3 (69%)	MLCT/ILCT/LLCT
	S_{28}	4.56	271.8	0.0350	H-2→L+5 (18%), H-1→L+4 (45%)	MLCT/ILCT
	S_{31}	4.67	265.3	0.2231	H-2→L+5 (27%), H-1→L+5 (21%)	MLCT/ILCT
	S_{32}	4.70	264.0	0.2235	H-2→L+5 (20%), H-1→L+5 (28%)	MLCT/ILCT
	S_{34}	4.76	260.6	0.0553	H-3→L+4 (60%), H-2→L+5 (10%)	MLCT/ILCT/LLCT
	S_{36}	4.80	258.2	0.0366	H-6→L+1 (58%), H-1→L+6 (23%)	ILCT/LLCT
	S_{41}	4.90	253.0	0.0901	H-4→L+4 (21%), H→L+8 (16%), H→L+9 (21%)	MLCT/ILCT
	S_{44}	4.96	250.1	0.0553	H→L+8 (48%), H→L+9 (20%)	MLCT/ILCT/LLCT
	S_{49}	5.05	245.5	0.0891	H-8→L (24%), H-3→L+6 (25%)	MLCT/ILCT/LLCT
	S_{57}	5.22	237.6	0.0362	H-9→L+1 (19%), H-7→L+2 (14%)	ILCT/LLCT
	S_{59}	5.25	236.0	0.0807	H-6→L+3 (67%)	ILCT
	T_1	2.77	448.2	0.0000	H-1→L+2 (15%), H→L (15%), H→L+1 (50%)	MLCT/ILCT

	T_2	2.82	440.0		0.0000	H→L (71%)	MLCT/ILCT/LLCT
	T_3	2.83	437.9		0.0000	H-1→L+1 (25%), H→L (11%), H→L+2 (34%)	MLCT/ILCT
6a	S_1	2.77	448.3		0.0004	H→L (98%)	MLCT/LLCT
	S_2	3.19	388.8		0.0437	H→L+1 (97%)	MLCT/ILCT/LLCT
	S_7	3.70	334.7		0.0338	H-3→L (23%), H→L+3 (62%)	MLCT/ILCT/LLCT
	S_{17}	4.14	299.6		0.0535	H-3→L+1 (18%), H-3→L+2 (32%), H→L+7 (15%)	MLCT/ILCT/LLCT
	S_{19}	4.17	297.4		0.0359	H-3→L+1(15%), H-3→L+2 (29%), H-2→L+2 (25%)	MLCT/ILCT/LLCT
	S_{20}	4.26	291.1		0.0710	H-4→L+1 (51%), H-2→L+1 (14%)	MLCT/ILCT/LLCT
	S_{21}	4.28	289.5		0.0519	H-5→L+1 (19%), H-1→L+3 (24%),	MLCT/ILCT
	S_{22}	4.32	286.8		0.2184	H-6→L (59%), H-2→L+3 (14%)	ILCT/LLCT
	S_{25}	4.43	279.8		0.0579	H-5→L+2 (34%), H-2→L+3 (18%)	MLCT/ILCT
	S_{26}	4.46	278.2		0.1012	H-5→L+2 (28%), H-2→L+3 (35%)	MLCT/ILCT/LLCT
	S_{27}	4.49	276.1		0.0358	H-1→L+4 (66%)	MLCT/ILCT/LLCT
	S_{28}	4.54	273.4		0.0632	H-4→L+3 (10%), H-3→L+3 (68%)	MLCT/ILCT/LLCT
	S_{29}	4.55	272.5		0.0342	H-4→L+4 (10%), H-2→L+4 (64%)	MLCT/ILCT/LLCT
	S_{32}	4.68	265.0		0.0932	H-1→L+6 (39%), H→L+8 (29%)	MLCT/ILCT/LLCT
	S_{33}	4.69	264.4		0.1327	H-1→L+6 (29%), H→L+8 (44%)	MLCT/ILCT/LLCT
	S_{34}	4.70	264.0		0.0357	H-4→L+3 (49%), H-2→L+3 (13%)	MLCT/ILCT/LLCT
	S_{36}	4.74	261.7		0.1129	H-2→L+5 (40%)	MLCT/ILCT/LLCT
	S_{37}	4.76	260.6		0.0437	H-7→L (45%)	MLCT/ILCT
	S_{38}	4.78	259.3		0.0516	H-4→L+4 (46%)	MLCT/ILCT/LLCT
	S_{41}	4.82	257.1		0.0326	H-6→L+1(21%), H-5→L+3 (38%), H-1→L+7 (17%)	MLCT/ILCT
	S_{43}	4.83	256.5		0.0424	H-8→L (15%), H-6→L+1 (49%)	ILCT/LLCT
	S_{44}	4.86	255.0		0.0581	H-3→L+5 (37%)	MLCT/ILCT/LLCT
	S_{46}	4.92	252.2		0.1579	H-6→L+2 (12%), H→L+9 (39%)	MLCT/ILCT
	S_{48}	4.94	250.9		0.0513	H-5→L+4 (53%)	MLCT/ILCT
	S_{58}	5.20	238.4		0.0621	H-10→L (27%), H-6→L+3 (38%)	ILCT
	T_1	2.72	456.0		0.0000	H→L (90%)	MLCT/LLCT
	T_2	2.79	443.9		0.0000	H-1→L+2 (16%), H→L+1 (57%)	MLCT/ILCT/LLCT
	T_3	2.83	437.6		0.0000	H-1→L+1 (26%), H→L+2 (49%)	MLCT/ILCT
7a	S_1	2.99	415.0	411	0.0007	H→L (99%)	MLCT/LLCT
	S_2	3.18	390.3	380	0.0626	H→L+1 (96%)	MLCT/LLCT
	S_3	3.28	378.5		0.0008	H→L+2 (97%)	MLCT/ILCT
	S_6	3.74	331.6		0.0444	H-2→L (24%), H-1→L (58%)	MLCT/LLCT
	S_9	3.90	318.1		0.0470	H-3→L (40%), H→L+5 (13%)	MLCT/ILCT/LLCT
	S_{12}	3.97	312.2		0.0857	H-2→L+1 (30%), H-1→L+2 (47%)	MLCT/ILCT/LLCT
	S_{16}	4.16	298.0		0.0904	H-3→L+2 (51%), H-1→L+2 (11%),	MLCT/ILCT
	S_{19}	4.26	291.2		0.0325	H-5→L (18%), H-2→L+3 (51%)	MLCT/ILCT
	S_{20}	4.31	287.8		0.1049	H-4→L+1 (52%), H-2→L+3 (10%)	MLCT/ILCT/LLCT
	S_{21}	4.33	286.4		0.0453	H-4→L+2 (36%), H-1→L+4 (19%)	MLCT/ILCT
	S_{28}	4.67	265.4		0.3452	H-2→L+5 (15%), H-1→L+5 (33%)	MLCT/ILCT
	S_{30}	4.72	262.6		0.0331	H-5→L+3 (37%), H-2→L+5 (14%)	MLCT/ILCT

	S_{31}	4.75	261.1		0.1598	H-5→L+3 (20%), H-2→L+5 (29%)	MLCT/ILCT
	S_{32}	4.79	258.9	253	0.2396	H-6→L (61%), H-3→L+4 (12%)	MLCT/ILCT
	S_{34}	4.90	253.2		0.0760	H-4→L+4 (49%), H→L+6 (30%)	MLCT/ILCT
	S_{35}	4.93	251.2		0.1806	H-4→L+4 (35%), H→L+6 (31%)	MLCT/ILCT
	S_{36}	4.97	249.6		0.0348	H-6→L+1 (16%), H→L+7 (29%)	MLCT/ILCT
	S_{44}	5.23	237.1		0.1435	H-6→L+3 (74%)	ILCT/LLCT
	S_{48}	5.34	232.2		0.0455	H-7→L+1 (29%), H→L+8 (24%)	MLCT/ILCT/LLCT
	S_{52}	5.44	227.8		0.0517	H→L+11 (37%), H→L+12 (16%)	MLCT/ILCT/LLCT
	T_1	2.79	444.9		0.0000	H-1→L+2 (16%), H→L+1 (63%)	MLCT/ILCT/LLCT
	T_2	2.83	438.0		0.0000	H-1→L+1 (24%), H→L+2 (53%)	MLCT/ILCT/LLCT
	T_3	2.96	419.3	411	0.0000	H→L (96%)	MLCT/LLCT
	T_4	3.24	382.9	380	0.0000	H→L+1 (13%), H→L+2 (21%)	MLCT/ILCT/LLCT

Table S10 Calculated excited energies, dominant orbital excitations, and oscillator strength (*f*) from PCM-TD -B3LYP calculations in CH_3CN media for **1b-7b**

	State	E_{th} eV	λ_{cal} nm	λ_{exp} nm	*f*	Excitation (contribution)	Character
1b	S_1	3.21	386.0		0.0014	H→L (97%)	MLCT/LLCT
	S_2	3.36	368.8		0.0444	H→L+1 (95%)	MLCT/ILCT
	S_7	3.91	317.3		0.0490	H-3→L (20%), H-2→L+1 (27%), H-1→L+1 (20%)	MLCT/ILCT/LLCT
	S_{10}	4.00	310.2		0.0568	H-4→L (17%), H-1→L+2 (49%)	MLCT/ILCT/LLCT
	S_{11}	4.01	309.0		0.0398	H-4→L (48%), H-1→L+2 (23%)	MLCT/ILCT/LLCT
	S_{15}	4.17	297.6		0.0431	H-4→L+1 (15%), H-3→L+2 (17%), H→L+5 (19%)	MLCT/ILCT
	S_{17}	4.25	291.9		0.0722	H-4→L+1 (24%), H-3→L+2 (22%), H→L+4 (17%)	MLCT/ILCT
	S_{18}	4.26	291.2		0.0548	H-4→L+2 (16%), H-3→L+2 (13%), H→L+5 (33%)	MLCT/ILCT
	S_{19}	4.32	287.3		0.0605	H-4→L+2 (34%), H-1→L+3 (11%), H→L+5 (20%)	MLCT/ILCT
	S_{20}	4.33	286.3		0.0335	H-5→L+1 (74%), H-4→L+2 (11%)	MLCT/ILCT
	S_{21}	4.39	282.3		0.1082	H-6→L (59%), H-2→L+3 (19%)	MLCT/ILCT/LLCT
	S_{22}	4.32	279.7		0.0325	H-1→L+3 (61%)	MLCT/ILCT/LLCT
	S_{24}	4.52	274.6		0.1963	H-6→L (25%), H-2→L+3 (46%)	MLCT/ILCT/LLCT
	S_{30}	4.71	263.4		0.1500	H-2→L+5 (16%), H-1→L+5 (26%)	MLCT/ILCT/LLCT
	S_{31}	4.73	261.9		0.0781	H-4→L+3 (66%)	MLCT/ILCT/LLCT
	S_{32}	4.76	260.6		0.1088	H-7→L (33%), H-6→L+2 (19%), H→L+7 (14%)	MLCT/ILCT
	S_{33}	4.77	259.9		0.1060	H-7→L (58%), H-6→L+2 (14%)	ILCT
	S_{34}	4.79	258.6		0.0428	H-6→L+2 (28%), H→L+7 (44%)	MLCT/ILCT
	S_{35}	4.82	257.4		0.0837	H-6→L+2 (17%), H-2→L+5 (14%), H→L+7 (29%)	MLCT/ILCT
	S_{42}	4.99	248.4		0.0362	H-8→L (50%), H-4→L+4 (17%)	MLCT/ILCT
	S_{43}	5.01	247.2		0.0525	H-4→L+5 (56%), H→L+8 (20%)	MLCT/ILCT
	S_{44}	5.02	247		0.1259	H-4→L+5 (19%), H→L+8 (23%)	MLCT/ILCT
	S_{47}	5.12	242.1		0.0391	H-10→L (10%), H-6→L+3 (46%)	MLCT/ILCT/LLCT
	S_{53}	5.20	238.4		0.0618	H-6→L+3 (13%), H-3→L+6 (11%)	MLCT/ILCT/LLCT
	T_1	2.89	429.1		0.0000	H-1→L+2 (24%), H→L+1 (44%)	MLCT/ILCT
	T_2	2.92	424.0		0.0000	H-2→L+2 (10%), H-1→L+1 (33%), H→L+2 (30%)	MLCT/ILCT
	T_3	3.15	393.5		0.0000	H-6→L (12%), H-3→L (24%), H→L (36%)	MLCT/ILCT/LLCT

2b	S_1	3.05	406.7	0.0017	H→L (98%)	MLCT/LLCT
	S_2	3.32	373.2	0.0464	H→L+1 (95%)	MLCT/LLCT
	S_4	3.53	351.2	0.0361	H-4→L (23%), H-2→L (72%)	LLCT/ILCT
	S_5	3.58	346.0	0.0376	H-1→L (89%)	LLCT
	S_6	3.80	326.7	0.0651	H-3→L (76%), H→L+3 (10%)	MLCT/ILCT/LLCT
	S_8	3.85	322.3	0.0447	H-4→L+1 (18%), H-2→L+1 (58%)	MLCT/ILCT/LLCT
	S_9	3.87	320.4	0.0838	H-5→L (27%), H-4→L (29%), H-1→L+1 (21%)	MLCT/ILCT/LLCT
	S_{11}	3.91	317.0	0.0863	H-5→L (49%), H-4→L (25%), H-2→L (13%)	MLCT/ILCT/LLCT
	S_{12}	3.99	310.5	0.0695	H-1→L+2 (76%)	MLCT/ILCT/LLCT
	S_{16}	4.13	299.8	0.0498	H-3→L+1 (27%), H→L+5 (39%)	MLCT/ILCT
	S_{19}	4.23	293.1	0.0388	H-4→L+1 (29%), H-3→L+2 (20%), H→L+5 (25%)	MLCT/ILCT
	S_{20}	4.25	291.8	0.0472	H-5→L+1 (47%), H-3→L+2 (19%)	MLCT/ILCT
	S_{21}	4.28	289.3	0.0679	H-5→L+2(20%), H-4→L+2 (16%), H-2→L+3 (26%)	MLCT/ILCT/LLCT
	S_{23}	4.34	285.9	0.1160	H-5→L+2(27%), H-2→L+3 (20%), H-1→L+3 (19%)	MLCT/ILCT
	S_{24}	4.35	284.8	0.0542	H-4→L+2 (34%), H-2→L+3 (23%)	MLCT/ILCT
	S_{34}	4.71	263.3	0.1222	H-7→L+1 (33%), H-1→L+5 (18%)	ILCT
	S_{35}	4.73	262.2	0.1769	H-2→L+5 (22%), H-1→L+5 (40%)	MLCT/ILCT
	S_{36}	4.74	261.5	0.1082	H-8→L (19%), H-7→L+1 (43%)	ILCT
	S_{37}	4.76	260.4	0.2163	H-8→L (52%)	MLCT/ILCT
	S_{43}	4.93	251.3	0.1701	H-4→L+4 (16%), H→L+7 (34%), H→L+8 (13%)	MLCT/ILCT/LLCT
	S_{44}	4.96	249.9	0.0673	H-5→L+4 (53%)	MLCT/ILCT
	S_{47}	5.05	245.6	0.0476	H-8→L+1 (29%), H→L+7 (19%), H→L+8 (20%)	MLCT/ILCT/LLCT
	S_{57}	5.24	236.7	0.0387	H-4→L+10 (18%), H→L+9 (11%)	MLCT/ILCT/LLCT
	T_1	2.87	432.5	0.0000	H-3→L (15%), H-2→L (59%)	ILCT/LLCT
	T_2	2.88	430.5	0.0000	H-1→L+2 (21%), H→L+1 (45%)	MLCT/ILCT/LLCT
	T_3	2.92	425.1	0.0000	H-1→L+1 (34%), H→L+2 (32%)	MLCT/ILCT/LLCT
3b	S_1	3.05	406.6	0.0018	H→L (98%)	MLCT/LLCT
	S_2	3.33	372.6	0.0445	H→L+1 (95%)	MLCT/ILCT/LLCT
	S_5	3.58	346.5	0.0467	H-1→L (88%)	LLCT
	S_6	3.79	326.8	0.0543	H-3→L (80%)	MLCT/ILCT/LLCT
	S_8	3.84	322.7	0.0392	H-4→L+1 (14%), H-2→L+1 (50%), H→L+3 (13%)	MLCT/ILCT
	S_{11}	3.91	316.8	0.0906	H-5→L (41%), H-4→L (34%), H-2→L (16%)	MLCT/ILCT/LLCT
	S_{12}	3.99	310.8	0.0666	H-1→L+2 (75%)	MLCT/ILCT/LLCT
	S_{13}	4.02	308.0	0.0333	H-2→L+2 (59%), H-1→L+1 (11%)	MLCT/ILCT/LLCT
	S_{16}	4.13	300.0	0.0417	H-6→L (85%)	MLCT/ILCT/LLCT
	S_{17}	4.14	299.4	0.0441	H-3→L+1 (36%), H→L+5 (37%)	MLCT/ILCT
	S_{19}	4.23	292.8	0.0392	H-4→L+1 (36%), H-3→L+2 (13%), H→L+5 (25%)	MLCT/ILCT/LLCT
	S_{20}	4.25	291.9	0.0544	H-5→L+1 (48%), H-3→L+2 (17%)	MLCT/ILCT
	S_{21}	4.29	289.2	0.0638	H-5→L+2 (36%), H-2→L+3 (14%)	MLCT/ILCT
	S_{23}	4.34	285.5	0.0683	H-5→L+2 (21%), H-2→L+3(17%), H-1→L+3 (22%)	MLCT/ILCT
	S_{24}	4.36	284.3	0.0725	H-4→L+2 (28%), H-2→L+3 (29%)	MLCT/ILCT/LLCT
	S_{36}	4.70	263.7	0.1566	H-7→L+1 (14%), H-1→L+5 (33%)	MLCT/ILCT/LLCT

	S_{38}	4.73	262.1	0.1178	H-2→L+5 (17%), H-1→L+5 (21%),	MLCT/ILCT/LLCT
	S_{39}	4.75	261.1	0.0888	H-10→L (17%), H-7→L+1 (40%)	ILCT/LLCT
	S_{40}	4.76	260.2	0.1746	H-10→L (29%), H-8→L (20%)	MLCT/ILCT
	S_{46}	4.92	252.0	0.0644	H→L+7 (18%), H→L+8 (56%)	MLCT/LLCT
	S_{47}	4.94	250.9	0.0479	H-4→L+4 (12%), H-2→L+6 (30%), H→L+9 (18%)	MLCT/ILCT
	S_{49}	4.97	249.7	0.0640	H-5→L+4 (41%), H→L+9 (20%)	MLCT/ILCT/LLCT
	S_{52}	5.02	246.7	0.0358	H-8→L+1 (49%)	MLCT/ILCT/LLCT
	S_{55}	5.07	244.5	0.0412	H-11→L (25%), H→L+10 (17%)	MLCT/ILCT/LLCT
	S_{58}	5.12	241.9	0.0761	H-2→L+7 (73%)	MLCT/ILCT/LLCT
	T_1	2.87	431.4	0.0000	H-3→L (20%), H-2→L (52%)	ILCT/LLCT
	T_2	2.88	430.1	0.0000	H-1→L+2 (21%), H→L+1 (43%)	MLCT/ILCT/LLCT
	T_3	2.92	424.9	0.0000	H-1→L+1 (33%), H→L+2 (32%)	MLCT/ILCT/LLCT
4b	S_1	3.03	408.6	0.0023	H→L (98%)	MLCT/LLCT
	S_2	3.39	365.5	0.0493	H→L+1 (95%)	MLCT/ILCT
	S_7	3.87	320.3	0.0916	H-5→L (69%), H-4→L (13%)	MLCT/ILCT/LLCT
	S_9	3.95	313.8	0.0415	H-3→L+1 (20%), H-2→L+1 (60%)	ILCT
	S_{12}	4.04	307.2	0.0978	H-4→L (33%), H-1→L+2 (41%)	MLCT/ILCT/LLCT
	S_{15}	4.18	296.3	0.0475	H-3→L+1 (35%), H-2→L+1 (18%), H→L+4 (12%)	MLCT/ILCT
	S_{16}	4.20	295.3	0.1076	H-6→L (17%), H-3→L+2 (13%), H→L+5 (36%)	MLCT/ILCT/LLCT
	S_{17}	4.21	294.7	0.2272	H-6→L (62%), H-5→L+1 (11%), H→L+5 (14%)	MLCT/ILCT
	S_{18}	4.26	291.1	0.0418	H-5→L+1(18%), H-3→L+2 (29%), H-2→L+2 (24%)	MLCT/ILCT
	S_{22}	4.37	283.5	0.0655	H→L+6 (62%)	MLCT/ILCT/LLCT
	S_{26}	4.51	274.6	0.0581	H-7→L (18%), H-3→L+3 (10%), H-2→L+3 (53%)	MLCT/ILCT/LLCT
	S_{30}	4.68	264.8	0.0581	H-3→L+3 (20%), H-2→L+4 (48%)	ILCT/LLCT
	S_{32}	4.75	261.1	0.0826	H-5→L+3 (47%), H-1→L+5 (17%)	MLCT/ILCT/LLCT
	S_{33}	4.75	260.9	0.1485	H-5→L+3 (13%), H-1→L+5 (48%)	MLCT/ILCT/LLCT
	S_{34}	4.80	258.5	0.0820	H-2→L+5 (28%), H-1→L+6 (47%)	MLCT/ILCT/LLCT
	S_{35}	4.83	256.9	0.0394	H-2→L+5 (18%), H-1→L+6 (29%), H→L+7 (12%)	MLCT/ILCT/LLCT
	S_{36}	4.85	255.6	0.0714	H→L+7 (43%)	MLCT/ILCT/LLCT
	S_{37}	4.87	254.8	0.0432	H-3→L+4 (51%)	MLCT/ILCT/LLCT
	S_{38}	4.89	253.7	0.0744	H-2→L+6 (53%), H→L+7 (13%)	MLCT/ILCT/LLCT
	S_{41}	4.96	250.1	0.0322	H-7→L+1 (57%), H-7→L+2 (11%)	ILCT/LLCT
	S_{42}	4.96	249.9	0.0626	H-9→L (11%), H-8→L (24%), H-7→L+1 (19%)	ILCT
	S_{44}	4.99	248.3	0.0654	H-3→L+5 (16%), H→L+8 (21%)	MLCT/ILCT/LLCT
	S_{47}	5.06	244.9	0.0840	H-5→L+4 (18%), H→L+9 (21%), H→L+11 (15%)	MLCT/ILCT
	S_{50}	5.13	241.8	0.0497	H-7→L+2 (42%), H-6→L+3 (17%)	ILCT/LLCT
	S_{51}	5.13	241.7	0.0688	H-7→L+2 (36%), H-6→L+3 (19%)	MLCT/ILCT/LLCT
	S_{52}	5.14	241.2	0.0344	H-5→L+5 (16%), H-4→L+5 (32%), H→L+8 (10%)	MLCT/ILCT/LLCT
	T_1	2.89	429.5	0.0000	H-1→L+2 (22%), H→L (10%), H→L+1 (39%)	MLCT/ILCT/LLCT
	T_2	2.93	423.6	0.0000	H-2→L+2 (10%), H-1→L+1 (34%), H→L+2 (30%)	MLCT/ILCT/LLCT
	T_3	3.02	411.2	0.0000	H→L (86%)	MLCT/LLCT
5b	S_1	3.07	403.6	0.0009	H→L (98%)	MLCT/LLCT

	S_2	3.38	366.9	0.0491	H→L+1 (95%)	MLCT/ILCT
	S_7	3.90	318.1	0.1089	H-4→L (51%), H-1→L+1 (25%)	MLCT/ILCT/LLCT
	S_9	3.94	314.4	0.0357	H-2→L+1 (33%), H→L+3 (47%)	MLCT/ILCT/LLCT
	S_{11}	4.03	307.8	0.0726	H-2→L+1 (10%), H-1→L+2 (73%)	ILCT
	S_{16}	4.18	296.3	0.0403	H-3→L+2 (16%), H-2→L+1 (12%), H→L+5 (24%)	MLCT/ILCT
	S_{17}	4.25	291.5	0.0444	H-4→L+1 (28%), H-3→L+2(21%), H-2→L+2 (23%)	MLCT/ILCT
	S_{18}	4.29	288.6	0.0649	H-4→L+2 (18%), H-3→L+2 (19%), H→L+5 (22%)	MLCT/ILCT
	S_{19}	4.34	285.7	0.0643	H-4→L+2 (30%), H-1→L+3 (13%), H→L+5 (21%)	MLCT/ILCT
	S_{21}	4.42	280.5	0.0663	H-6→L (39%), H-2→L+3 (12%), H-1→L+3 (25%)	MLCT/ILCT/LLCT
	S_{22}	4.44	279.1	0.0618	H-6→L (21%), H-1→L+3 (33%), H→L+6 (16%)	MLCT/ILCT/LLCT
	S_{25}	4.51	274.6	0.1667	H-6→L (22%), H-3→L+3 (11%), H-2→L+3 (51%)	MLCT/ILCT/LLCT
	S_{30}	4.72	262.5	0.0576	H-4→L+3 (46%), H-1→L+5 (19%)	MLCT/ILCT/LLCT
	S_{31}	4.74	261.5	0.1598	H-4→L+3 (23%), H-1→L+5 (36%)	MLCT/ILCT/LLCT
	S_{32}	4.80	258.6	0.0393	H-2→L+5 (18%), H→L+7 (59%)	MLCT/ILCT/LLCT
	S_{33}	4.83	256.9	0.1884	H-2→L+5 (32%), H-1→L+5 (15%), H→L+7 (20%)	MLCT/ILCT
	S_{34}	4.85	255.7	0.0341	H-6→L+1 (70%), H-1→L+6 (10%)	ILCT/LLCT
	S_{41}	4.97	249.3	0.1016	H-4→L+4 (15%), H→L+8 (14%), H→L+9 (30%)	MLCT/ILCT
	S_{42}	5.00	248.2	0.0814	H-3→L+6 (11%), H-2→L+6 (29%)	ILCT/LLCT
	S_{44}	5.03	246.4	0.033	H-8→L (35%), H-2→L+6 (29%)	MLCT/ILCT/LLCT
	S_{45}	5.05	245.5	0.0697	H-4→L+4 (13%), H-4→L+5 (30%)	MLCT/ILCT
	S_{56}	5.26	235.8	0.0603	H-3→L+11 (19%), H→L+10 (14%)	ILCT/LLCT
	S_{58}	5.32	233.1	0.0318	H-6→L+3 (33%), H-2→L+7 (19%)	ILCT/LLCT
	S_{60}	5.35	231.7	0.0351	H-8→L+1 (72%)	ILCT/LLCT
	T_1	2.89	428.5	0.0000	H-1→L+2 (24%), H→L+1 (45%)	MLCT/ILCT
	T_2	2.93	423.7	0.0000	H-1→L+1 (35%), H→L+2 (32%)	MLCT/ILCT
	T_3	3.04	407.9	0.0000	H→L (88%)	MLCT/LLCT
6b	S_1	3.00	413.4	0.0002	H→L (98%)	MLCT/LLCT
	S_2	3.40	364.8	0.0426	H→L+1 (95%)	MLCT/ILCT/LLCT
	S_7	3.83	323.7	0.0515	H-5→L (29%), H-4→L (31%), H-3→L (27%)	MLCT/LLCT
	S_{10}	4.01	309.3	0.0402	H-5→L (56%), H-4→L (12%), H-3→L (14%)	MLCT/LLCT
	S_{11}	4.01	308.9	0.0314	H-2→L+1 (45%), H-1→L+1 (13%)	MLCT/ILCT/LLCT
	S_{13}	4.09	303.3	0.0654	H-1→L+2 (45%), H→L+4 (29%)	MLCT/ILCT/LLCT
	S_{14}	4.13	299.9	0.0322	H-2→L+2 (57%)	MLCT/ILCT/LLCT
	S_{19}	4.30	288.5	0.0764	H-3→L+1 (26%), H-3→L+2 (37%)	MLCT/ILCT/LLCT
	S_{20}	4.33	286.3	0.0711	H-4→L+1 (14%), H-4→L+2 (40%)	MLCT/ILCT
	S_{21}	4.36	284.3	0.0701	H-6→L (14%), H-5→L+1 (35%), H→L+6 (16%)	MLCT/ILCT
	S_{22}	4.38	283.3	0.2426	H-6→L (62%)	MLCT/ILCT
	S_{26}	4.51	274.9	0.0488	H-2→L+3 (73%)	MLCT/ILCT/LLCT
	S_{27}	4.57	271.1	0.0496	H-2→L+4 (12%), H-1→L+4 (61%)	MLCT/ILCT/LLCT
	S_{28}	4.65	266.9	0.034	H-2→L+4 (54%), H-1→L+4 (15%)	MLCT/ILCT/LLCT
	S_{29}	4.68	265.1	0.0545	H-4→L+3 (19%), H-3→L+3(36%), H-2→L+4 (14%)	MLCT/ILCT/LLCT
	S_{31}	4.73	262.1	0.0372	H-2→L+5 (15%), H-1→L+5 (47%)	MLCT/ILCT/LLCT
	S_{32}	4.78	259.4	0.1843	H-2→L+6 (10%), H-1→L+6 (60%)	MLCT/ILCT/LLCT

	S_{34}	4.81	257.9		0.0511	H-2→L+6 (15%), H-1→L+7 (15%), H→L+8 (21%)	MLCT/ILCT/LLCT
	S_{38}	4.85	255.7		0.0886	H-6→L+1 (53%), H-2→L+6 (15%)	ILCT/LLCT
	S_{39}	4.86	255.1		0.0315	H-5→L+4 (15%), H-4→L+4 (44%)	MLCT/ILCT/LLCT
	S_{41}	4.89	253.3		0.1044	H-2→L+7 (21%), H-1→L+7 (30%)	MLCT/ILCT/LLCT
	S_{45}	4.98	249.2		0.1147	H-3→L+6 (13%), H-1→L+7 (13%), H→L+9 (34%)	MLCT/ILCT/LLCT
	S_{48}	5.02	247.1		0.0798	H-4→L+5 (20%), H-3→L+5(25%), H-2→L+7 (21%)	MLCT/ILCT/LLCT
	S_{54}	5.16	240.0		0.0453	H-11→L (12%), H-3→L+7 (28%)	MLCT/ILCT/LLCT
	S_{59}	5.24	236.6		0.0581	H-6→L+3 (30%), H-3→L+7 (20%)	MLCT/ILCT
	T_1	2.91	426.6		0.0000	H-1→L+2 (22%), H→L+1 (46%)	MLCT/ILCT/LLCT
	T_2	2.92	423.7		0.0000	H-1→L+1 (26%), H→L (24%), H→L+2 (27%)	MLCT/ILCT/LLCT
	T_3	2.95	420.8		0.0000	H→L (60%), H→L+2 (13%)	MLCT/ILCT/LLCT
7b	S_1	3.23	384.3	387	0.0005	H→L (98%)	MLCT/LLCT
	S_2	3.38	366.3	360	0.0574	H→L+1 (95%)	MLCT/LLCT
	S_4	3.76	329.8		0.0355	H-3→L (16%), H-1→L (74%)	LLCT
	S_8	3.98	311.2		0.0389	H-3→L (30%), H-2→L (19%)	ILCT/LLCT
	S_{10}	4.04	306.5		0.0904	H-2→L+1 (30%), H-1→L+2 (21%)	MLCT/ILCT/LLCT
	S_{11}	4.05	306.1		0.0784	H-4→L (52%), H-1→L+2 (12%)	MLCT/ILCT/LLCT
	S_{13}	4.13	300.3		0.0265	H-2→L+2 (37%), H-1→L+1 (15%)	MLCT/ILCT/LLCT
	S_{18}	4.29	289.3		0.1792	H-3→L+2 (33%)	MLCT/ILCT
	S_{20}	4.33	286.2		0.0604	H-4→L+1 (21%), H-4→L+2 (29%)	MLCT/ILCT
	S_{21}	4.38	283.2		0.0486	H-3→L+3 (19%), H-2→L+3 (58%)	MLCT/ILCT/LLCT
	S_{27}	4.73	262.0		0.0392	H-2→L+4 (31%), H-1→L+5 (33%)	MLCT/ILCT
	S_{28}	4.76	260.6		0.3376	H-2→L+4 (26%), H-1→L+5 (29%)	MLCT/ILCT
	S_{29}	4.78	259.2		0.2396	H-6→L (52%), H-4→L+3 (22%)	MLCT/ILCT
	S_{30}	4.83	256.8		0.0305	H-5→L+3 (87%)	MLCT/ILCT
	S_{31}	4.84	256.4		0.0771	H-2→L+5 (58%)	MLCT/ILCT
	S_{34}	4.96	250.1		0.0327	H-6→L+1 (78%), H-4→L+4 (14%)	MLCT/ILCT
	S_{36}	4.98	249.1	250	0.2762	H→L+6 (52%)	MLCT/ILCT/LLCT
	S_{42}	5.24	236.7		0.1316	H-6→L+3 (79%)	ILCT/LLCT
	S_{44}	5.29	234.2		0.0321	H→L+7 (24%), H→L+8 (29%)	MLCT/ILCT
	S_{47}	5.41	229.0		0.0414	H→L+7 (21%), H→L+9 (21%)	MLCT/ILCT/LLCT
	S_{49}	5.45	227.7		0.0405	H-7→L (20%), H-1→L+6 (16%)	MLCT/LLCT
	S_{51}	5.50	225.4		0.0895	H-1→L+6 (17%), H→L+10 (26%)	MLCT/ILCT/LLCT
	S_{52}	5.53	224.1		0.0469	H-1→L+6 (17%), H→L+11 (16%)	MLCT/ILCT/LLCT
	T_1	2.91	426.0		0.0000	H-1→L+2 (23%), H→L+1 (48%)	MLCT/ILCT/LLCT
	T_2	2.94	422.2		0.0000	H-1→L+1 (33%), H→L+2 (38%)	MLCT/ILCT/LLCT
	T_3	3.19	388.8	387	0.0000	H→L (93%)	MLCT/LLCT
	T_4	3.35	370.1		0.0000	H-4→L (19%), H-3→L (21%)	MLCT/ILCT/LLCT
	T_5	3.38	366.3	360	0.0000	H-2→L+1 (24%), H→L+1 (40%)	MLCT/ILCT/LLCT

Table S11 Calculated unpaired-electron spin density distribution for **1a-7a** and **1b-7b**

Parameter	**1a**	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**
Ir	0.20	0.44	0.44	0.47	0.21	0.50	0.51
N^N^n	0.01	1.10	1.10	1.01	0.01	1.01	0.79
ppy1	0.01	0.16	0.16	0.17	0.01	0.16	0.27
ppy2	1.78	0.30	0.30	0.35	1.77	0.32	0.42
	1b	**2b**	**3b**	**4b**	**5b**	**6b**	**7b**
Ir	0.12	0.06	0.05	0.34	0.42	0.44	0.54
N^N^n	0.01	1.92	1.92	1.26	1.29	1.15	0.81
ppy1	0.00	0.00	0.00	0.12	0.11	0.13	0.27
ppy2	1.87	0.02	0.02	0.28	0.19	0.27	0.38

Table S1 Calculated net spin value located on Ir of MLCT and ^{3}MC states using B3LYP functional for **1-1e** and **2-2e**

Spin(Ir)	**1a**	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**
MLCT							
^{3}MC	1.543	1.359	1.528	1.356	1.388	1.500	1.397
Spin(Ir)	**1b**	**2b**	**3b**	**4b**	**5b**	**6b**	**7b**
MLCT							
^{3}MC	1.537	1.532	1.517	1.524	1.549	1.595	1.508

Table S12 Cartesian coordinates for the optimized structures for **1a**, **7a** and **7b** in the S_0 and T_1 states.

Optimized S_0 structure for $[Ir(ppy^0)_2(N\hat{}N^1)]^+$ (1a)

Ir	0.39277600	-0.08175300	-0.09302600	C	1.77321200	0.89182600	4.42734400
N	1.95912200	1.26706600	-0.84972100	H	2.09973500	1.07451800	5.44640400
N	-0.62127900	1.86068100	-0.47400000	C	2.25512900	-0.19925100	3.72544100
N	-1.82434500	2.42353100	-0.27959500	H	2.95855000	-0.88068800	4.18906600
N	0.94335100	0.41309800	1.82717900	C	1.83119300	-0.43553400	2.41373000
N	-0.17054200	-0.82087000	-1.92510600	C	2.25038400	-1.54536400	1.56821100
C	3.23535400	0.90438700	-1.03686000	C	1.64699300	-1.58940600	0.28851600
H	3.46738600	-0.13060800	-0.80580100	C	2.02118300	-2.63261000	-0.56530900
C	4.20090100	1.78787400	-1.49895400	H	1.58014700	-2.71170700	-1.55448700
H	5.22112500	1.44658800	-1.63452300	C	2.95639800	-3.58715200	-0.16934400
C	3.83033600	3.09998200	-1.77837500	H	3.22738400	-4.38821700	-0.85191300
H	4.55969100	3.81673900	-2.14236100	C	3.54286500	-3.52851300	1.09473000
C	2.50963700	3.48100900	-1.58608400	H	4.26855900	-4.27595000	1.39891000
H	2.18590700	4.49428700	-1.79681600	C	3.18890400	-2.50683300	1.96295900
C	1.59353900	2.54018200	-1.11795200	H	3.64860100	-2.46320200	2.94637500
C	0.19011200	2.85134100	-0.87883800	C	0.35752800	-0.43691100	-3.09878100
C	-0.51148500	4.06686700	-0.94811400	H	1.10397400	0.34682600	-3.04738500
H	-0.14489500	5.03881900	-1.24040700	C	-0.01018900	-1.00476400	-4.30461400
C	-1.79186000	3.74935100	-0.55782400	H	0.44762100	-0.66151100	-5.22519200
H	-2.68725300	4.34751600	-0.47619300	C	-0.96793600	-2.01838200	-4.29415200
C	-2.97271000	1.70093500	0.16145800	H	-1.27895600	-2.49438500	-5.21894900
C	-3.60018200	2.10509700	1.33720100	C	-1.52009400	-2.41139400	-3.08759000
H	-3.18531600	2.92097900	1.92201000	H	-2.26625100	-3.19670900	-3.05788000
C	-4.75427700	1.44616600	1.74796700	C	-1.11637100	-1.80222200	-1.89361000
H	-5.25145800	1.75245300	2.66282000	C	-1.63436900	-2.09575400	-0.56614600
C	-5.26308800	0.39483700	0.99000300	C	-1.08281300	-1.31571600	0.47854100
H	-6.16208600	-0.11994000	1.31414500	C	-1.58566000	-1.52137500	1.76713200
C	-4.62445600	0.00325700	-0.18427700	H	-1.19207400	-0.94872800	2.60205900
H	-5.02153400	-0.81673900	-0.77297500	C	-2.58913300	-2.45564300	2.00826900
C	-3.47604200	0.66000800	-0.61078800	H	-2.96115400	-2.59505900	3.01997000
H	-2.97628900	0.37942800	-1.53134600	C	-3.11427500	-3.22521700	0.96842000
C	0.47558800	1.46923900	2.51128000	H	-3.88582000	-3.96264000	1.16636000
H	-0.23546500	2.09355900	1.98418900	C	-2.63590900	-3.04425500	-0.31966700
C	0.86190100	1.74711000	3.80970600	H	-3.04422500	-3.64552200	-1.12771200
H	0.45433500	2.61134700	4.32151600				

Optimized T_1 structure for $[Ir(ppy^0)_2(N\hat{}N^1)]^+$ (1a)

Ir	0.38387400	-0.09696400	-0.09616800	C	2.31821800	0.68817200	4.26334100
N	1.90586700	1.27929300	-0.94529500	H	2.76807000	0.82555400	5.24174100
N	-0.63051600	1.89527500	-0.34299300	C	2.67516200	-0.39422000	3.47777300
N	-1.81016600	2.46052600	-0.04711200	H	3.40482900	-1.11187500	3.83385800
N	1.16828600	0.32175300	1.77075800	C	2.09157700	-0.57148200	2.21913600
N	-0.37133500	-0.71827300	-1.87974100	C	2.38367400	-1.65460700	1.28776700
C	3.15431000	0.90768100	-1.25673400	C	1.64669000	-1.63166900	0.07974800
H	3.38185100	-0.14402900	-1.11377800	C	1.89799900	-2.63473200	-0.86121600
C	4.10122800	1.80297500	-1.73459500	H	1.34692100	-2.65162100	-1.79646800
H	5.09922600	1.45340600	-1.97419200	C	2.84588600	-3.62524100	-0.61248800
C	3.73996600	3.13696400	-1.89567000	H	3.02367200	-4.39711500	-1.35634100
H	4.45456500	3.86394300	-2.26858300	C	3.56408500	-3.63899600	0.58374300
C	2.44744100	3.52732200	-1.57370200	H	4.29909200	-4.41492800	0.77260000
H	2.13149600	4.55801000	-1.69074800	C	3.33345600	-2.65429100	1.53285800
C	1.54923800	2.57327000	-1.09788100	H	3.89690500	-2.66977700	2.46150100
C	0.17398200	2.89463200	-0.73565400	C	0.00602900	-0.30433400	-3.09230100
C	-0.50746400	4.12291300	-0.68727600	H	0.76320700	0.47230300	-3.11290900
H	-0.14151400	5.10573400	-0.94168200	C	-0.50534100	-0.82631200	-4.26925200
C	-1.76990000	3.80050800	-0.24464900	H	-0.15342700	-0.44398400	-5.21999900
H	-2.64940300	4.40532700	-0.08026400	C	-1.47151700	-1.86700100	-4.19790300
C	-2.95812600	1.71550600	0.35547100	H	-1.87139800	-2.30850400	-5.10433900
C	-3.55733800	2.01707300	1.57549000	C	-1.88339500	-2.29954600	-2.96852200
H	-3.11814500	2.76706100	2.22679600	H	-2.61933600	-3.09193700	-2.88393900
C	-4.71467500	1.33911400	1.94389300	C	-1.36078000	-1.71976100	-1.77489900
H	-5.19045400	1.56454100	2.89298600	C	-1.74235000	-2.01972900	-0.46398900
C	-5.25578700	0.37271000	1.09949500	C	-1.05689700	-1.24399700	0.59825300
H	-6.15882800	-0.15467200	1.39058800	C	-1.43438500	-1.46536300	1.92553400
C	-4.64561500	0.08488600	-0.11897400	H	-0.94253600	-0.91226900	2.72024600
H	-5.07047900	-0.66482900	-0.77820100	C	-2.41910800	-2.38470100	2.25504600
C	-3.49330300	0.76114400	-0.50394300	H	-2.70574500	-2.54370400	3.28927800
H	-3.01567700	0.56058000	-1.45702900	C	-3.04546200	-3.15773500	1.22432000
C	0.82601600	1.37205500	2.53283000	H	-3.79325100	-3.89547900	1.50296500
H	0.08096900	2.03715000	2.11177600	C	-2.71998400	-2.99554800	-0.09221000
C	1.37434900	1.59499400	3.78287500	H	-3.20490400	-3.60426800	-0.84860400
H	1.06377800	2.45564600	4.36409200				

Optimized S_0 structure for $[Ir(ppy^0)_2(N\hat{}N^7)]^+$ (7a)

Ir	0.04451300	-0.01078100	-0.05626600	C	2.88075700	0.09434200	-0.61991000
N	-1.68612800	-1.07194300	0.78869800	C	1.66311400	0.71906700	-0.98110000
N	-0.33878600	-1.66445400	-1.39465100	C	1.71628900	1.72374300	-1.95263200
N	-1.36454900	-2.47051800	-1.03052400	H	0.80942000	2.24240000	-2.24947700
N	1.50036000	-1.14698100	0.85182000	C	2.92204300	2.08270600	-2.55038800
N	-1.26852600	1.30902200	-0.92989900	H	2.93610900	2.86803700	-3.30147900
C	-2.36137000	-0.69096300	1.88461800	C	4.11278200	1.44980800	-2.19118500
H	-1.96611400	0.18822200	2.38381200	H	5.04910400	1.73509400	-2.65993400
C	-3.47652000	-1.37211300	2.34437400	C	4.09181200	0.45688600	-1.22435400
H	-3.98938500	-1.03193700	3.23661500	H	5.02125700	-0.03077100	-0.94368000
C	-3.91410600	-2.48795400	1.63438800	C	-1.89316400	1.09873700	-2.09984000
H	-4.78571000	-3.04575100	1.96138500	H	-1.66323100	0.16191500	-2.59454900
C	-3.23061100	-2.88489200	0.49380900	C	-2.76447000	2.01800300	-2.65412800
H	-3.56087600	-3.74270800	-0.07927100	H	-3.24212800	1.80566400	-3.60370600
C	-2.11768600	-2.14338900	0.10827500	C	-2.99747300	3.20789200	-1.96503500
C	-1.48251900	-3.51812100	-1.89500700	H	-3.67318000	3.95598800	-2.36790100
H	-2.23905700	-4.27775200	-1.77442000	C	-2.35048600	3.42907500	-0.76170500
C	-0.49852500	-3.37555900	-2.84057200	H	-2.51021800	4.35151700	-0.21589500
H	-0.29960200	-4.02997800	-3.67544200	C	-1.47501500	2.46755900	-0.24527400
C	0.19209700	-2.20099800	-2.48206700	C	-0.71327500	2.57863300	0.99162500
H	1.04022300	-1.72151100	-2.95081000	C	0.14281300	1.48492900	1.27047500
C	1.27303000	-2.04604200	1.82264000	C	0.91284600	1.55263500	2.43677800
H	0.24011400	-2.15487000	2.13263600	H	1.59608200	0.74534000	2.68394700
C	2.28496200	-2.78327500	2.40860200	C	0.82956900	2.64815700	3.29333300
H	2.05184800	-3.49467700	3.19247500	H	1.44155700	2.67621700	4.19098300
C	3.59223200	-2.57913800	1.96717900	C	-0.02576900	3.71307700	3.00770300
H	4.41547300	-3.13724200	2.40226200	H	-0.08479100	4.56473000	3.67784500
C	3.83033400	-1.64971300	0.97022000	C	-0.79607600	3.67852300	1.85561800
H	4.83979000	-1.46939900	0.61998700	H	-1.45715800	4.51168800	1.63356900
C	2.77011700	-0.92594800	0.41279700				

Optimized T_1 structure for $[Ir(ppy^0)_2(N\hat{}N^7)]^+$ (7a)

Ir	0.02850200	-0.09036500	-0.02032600	C	-1.99854500	-2.08635400	-0.44922100
N	0.43104000	1.97881900	0.52858600	C	-0.68493300	-1.73447900	-0.87383700
N	-0.93611200	1.13989800	-1.53642900	C	-0.05584900	-2.54485500	-1.83356300
N	-0.81939600	2.47929300	-1.35919100	H	0.94091300	-2.29271700	-2.18236800
N	-1.79784300	-0.16872700	0.92302400	C	-0.69000600	-3.67184500	-2.33875000
N	1.86089800	-0.13854100	-0.93289800	H	-0.18953200	-4.29374100	-3.07509800
C	1.07080600	2.38942500	1.65950800	C	-1.97477700	-4.01159600	-1.90160000
H	1.61775500	1.61552800	2.18772300	H	-2.46841500	-4.89232400	-2.30040300
C	1.03800900	3.68028400	2.11531600	C	-2.62618800	-3.22426500	-0.95834000
H	1.59058600	3.94506900	3.00932700	H	-3.62079100	-3.50813200	-0.62793500
C	0.27599600	4.64767100	1.40673400	C	2.11511200	0.34315800	-2.16007700
H	0.19217500	5.66587100	1.76866100	H	1.26871200	0.76739800	-2.68810900
C	-0.37247200	4.25877000	0.25325100	C	3.37861400	0.29347500	-2.72135300
H	-0.97746100	4.96005700	-0.31210500	H	3.53933900	0.69587800	-3.71496900
C	-0.25524500	2.93693600	-0.17998200	C	4.41967000	-0.27698100	-1.98661100
C	-1.34260600	3.14499100	-2.42748500	H	5.42107400	-0.33629400	-2.40024100
H	-1.30198200	4.22046800	-2.49445000	C	4.15699500	-0.76565700	-0.71627300
C	-1.81745200	2.19077800	-3.31209000	H	4.95041500	-1.20795900	-0.12479700
H	-2.29386900	2.37311700	-4.26330000	C	2.86742500	-0.68350100	-0.19001500
C	-1.53650000	0.95799600	-2.72611500	C	2.44513100	-1.13273800	1.12727800
H	-1.72725400	-0.04384800	-3.08157400	C	1.05831400	-0.93505700	1.42360100
C	-2.22807600	0.72531300	1.82559700	C	0.58324400	-1.35848700	2.68231900
H	-1.53415300	1.52108200	2.07263600	H	-0.46389700	-1.22271400	2.93403500
C	-3.48037800	0.63530200	2.40883700	C	1.43238300	-1.94809700	3.60422000
H	-3.78911000	1.37869500	3.13470000	H	1.05251000	-2.26877700	4.56954300
C	-4.31491900	-0.41934400	2.04055100	C	2.78705800	-2.13418200	3.29383600
H	-5.30233900	-0.52136400	2.47943100	H	3.44966100	-2.59557100	4.01960000
C	-3.86922100	-1.33885300	1.10436900	C	3.29035100	-1.73244700	2.06116200
H	-4.50370400	-2.16413200	0.80286400	H	4.34124000	-1.89355800	1.84070700
C	-2.59805000	-1.20188100	0.54366400				

Optimized S_0 structure for $[Ir(ppy^1)_2(N\hat{}N^7)]^+$ (7b)

Ir	0.18749000	-0.23252700	-0.07405300	H	2.65769300	3.90013900	-3.49087500
F	-1.42137400	2.79399500	4.08428900	C	1.67008800	3.43448000	-1.64625200
F	0.86197800	4.93174700	0.63326000	H	1.67537300	4.45220100	-1.28363300
F	-3.61037100	1.59150200	-3.43134600	C	1.09218400	2.43036900	-0.85785000
F	-4.92740600	-1.44038600	-0.15013100	C	0.45850000	2.59702000	0.44186500
N	0.76388600	-1.98607900	-1.18691900	C	-0.09354600	1.41914900	1.01536100
N	1.97796500	-2.49395600	-0.86544000	C	-0.72866000	1.50457800	2.25412400
N	2.18653600	-0.76033200	0.65663600	H	-1.17794500	0.64036000	2.73019200
N	1.07987000	1.14461400	-1.31214000	C	-0.81094200	2.73060800	2.90214700
N	-0.87967000	-1.45769000	1.18644000	C	-0.27996100	3.89834400	2.37168500
C	0.23880500	-2.80702100	-2.08303900	H	-0.35484000	4.84583700	2.89054100
H	-0.74305700	-2.59901200	-2.48462400	C	0.34601000	3.80437300	1.14394600
C	1.12323100	-3.86816500	-2.35780100	C	-0.34474700	-2.12007600	2.22456200
H	0.97536800	-4.69092800	-3.04044200	H	0.71804500	-1.97534200	2.38029400
C	2.21942700	-3.63864300	-1.56514400	C	-1.09198800	-2.92958400	3.05889400
H	3.13290400	-4.20018700	-1.44636500	H	-0.61513200	-3.43989400	3.88778100
C	2.76678500	-1.82494400	0.08346800	C	-2.45574800	-3.05745200	2.80185800
C	4.05533900	-2.24492300	0.39980300	H	-3.08046400	-3.68133200	3.43350700
H	4.50126500	-3.10418900	-0.08614700	C	-3.01514900	-2.37703000	1.73398700
C	4.75977200	-1.52381900	1.35332900	H	-4.07113400	-2.45709600	1.52026200
H	5.76684000	-1.82609600	1.62190200	C	-2.21277100	-1.56509400	0.92053100
C	4.16701300	-0.41434800	1.95142900	C	-2.64736400	-0.77202200	-0.21864200
H	4.68953600	0.17377400	2.69701100	C	-1.63980300	0.00412200	-0.85134300
C	2.88195000	-0.06519600	1.57134300	C	-1.98416300	0.80456200	-1.93940200
H	2.36392200	0.78882300	1.99541800	H	-1.25761400	1.42573900	-2.45061500
C	1.60772600	0.84692800	-2.51021700	C	-3.29823800	0.82336200	-2.38875000
H	1.54091200	-0.19318600	-2.80840400	C	-4.30589400	0.07230800	-1.79914100
C	2.18574000	1.80032700	-3.32721500	H	-5.32528000	0.10021300	-2.16323600
H	2.59388800	1.51298300	-4.28936100	C	-3.95497700	-0.71277800	-0.71859300
C	2.21595700	3.11959000	-2.87924100				

Optimized T_1 structure for $[Ir(ppy^1)_2(N\hat{}N^7)]^+$ (7b)

Ir	0.00251400	0.20281100	-0.08985900				
F	-2.03807900	-1.98179900	4.36217100	C	-3.39078000	-1.99088000	2.45670000
F	-4.70714000	-1.98748000	0.54425700	H	-4.18317100	-2.49710500	2.99560700
F	1.21544400	-4.21226300	-2.92316900	C	-3.54870700	-1.65621100	1.12121700
F	4.03962100	-3.06462400	0.59774000	C	1.59524400	1.23920000	2.25351400
N	1.30195200	1.41964200	-1.34895300	H	0.80469600	1.98159600	2.25815200
N	1.11064100	2.75780500	-1.25593600	C	2.63696700	1.26972900	3.16481900
N	-0.63768300	2.25764000	0.17739200	H	2.67622900	2.05604000	3.90975700
N	-1.50345800	-0.00699600	-1.46061200	C	3.61067900	0.27621500	3.09364400
N	1.49804300	0.28581600	1.31545600	H	4.44181000	0.26703000	3.79162400
C	2.21214900	1.22558500	-2.31893100	C	3.51276600	-0.70894600	2.12263000
H	2.51643800	0.22205300	-2.57722100	H	4.25721200	-1.48884700	2.05119200
C	2.61782500	2.45141800	-2.84384600	C	2.43982000	-0.69572600	1.22601500
H	3.33501200	2.62412500	-3.63175300	C	2.18396300	-1.65158000	0.15605100
C	1.89373100	3.41165400	-2.15701900	C	1.02324000	-1.41576200	-0.64044900
H	1.84507300	4.48322300	-2.26933600	C	0.70746400	-2.28277100	-1.69263100
C	0.22231600	3.22151300	-0.29784800	H	-0.15828200	-2.12327700	-2.32535600
C	0.19812100	4.54415700	0.14016000	C	1.51500200	-3.38300900	-1.92941300
H	0.94106000	5.24618500	-0.22469000	C	2.64349700	-3.65347800	-1.16059000
C	-0.77039100	4.93524500	1.04348200	H	3.26452300	-4.51954400	-1.35676500
H	-0.80512700	5.95498200	1.40844500	C	2.95381700	-2.78240100	-0.12895400
C	-1.70730900	3.96496000	1.49123900	C	-3.54870700	-1.65621100	1.12121700
H	-2.50921900	4.23164800	2.17012700	C	1.59524400	1.23920000	2.25351400
C	-1.59675900	2.67187400	1.05783800	H	0.80469600	1.98159600	2.25815200
H	-2.27826600	1.89939400	1.39745100	C	2.63696700	1.26972900	3.16481900
C	-1.43212700	0.43316600	-2.72583900	H	2.67622900	2.05604000	3.90975700
H	-0.50199800	0.91288600	-3.00793800	C	3.61067900	0.27621500	3.09364400
C	-2.47767200	0.27551600	-3.61905400	H	4.44181000	0.26703000	3.79162400
H	-2.37761600	0.64693900	-4.63250000	C	3.51276600	-0.70894600	2.12263000
C	-3.63822400	-0.36125200	-3.18363900	H	4.25721200	-1.48884700	2.05119200
H	-4.47577600	-0.50614600	-3.85822900	C	2.43982000	-0.69572600	1.22601500
C	-3.71802100	-0.80930600	-1.87280700	C	2.18396300	-1.65158000	0.15605100
H	-4.60988000	-1.30038400	-1.51011300	C	1.02324000	-1.41576200	-0.64044900
C	-2.63723500	-0.61849100	-1.00787200	C	0.70746400	-2.28277100	-1.69263100
C	-2.55577400	-1.00055800	0.39208800	H	-0.15828200	-2.12327700	-2.32535600
C	-1.32643700	-0.67904000	1.05811300	C	1.51500200	-3.38300900	-1.92941300
C	-1.16336300	-1.01881500	2.41315200	C	2.64349700	-3.65347800	-1.16059000
H	-0.25019500	-0.79127000	2.95064100	H	3.26452300	-4.51954400	-1.35676500
C	-2.18733200	-1.66164000	3.08150000	C	2.95381700	-2.78240100	-0.12895400

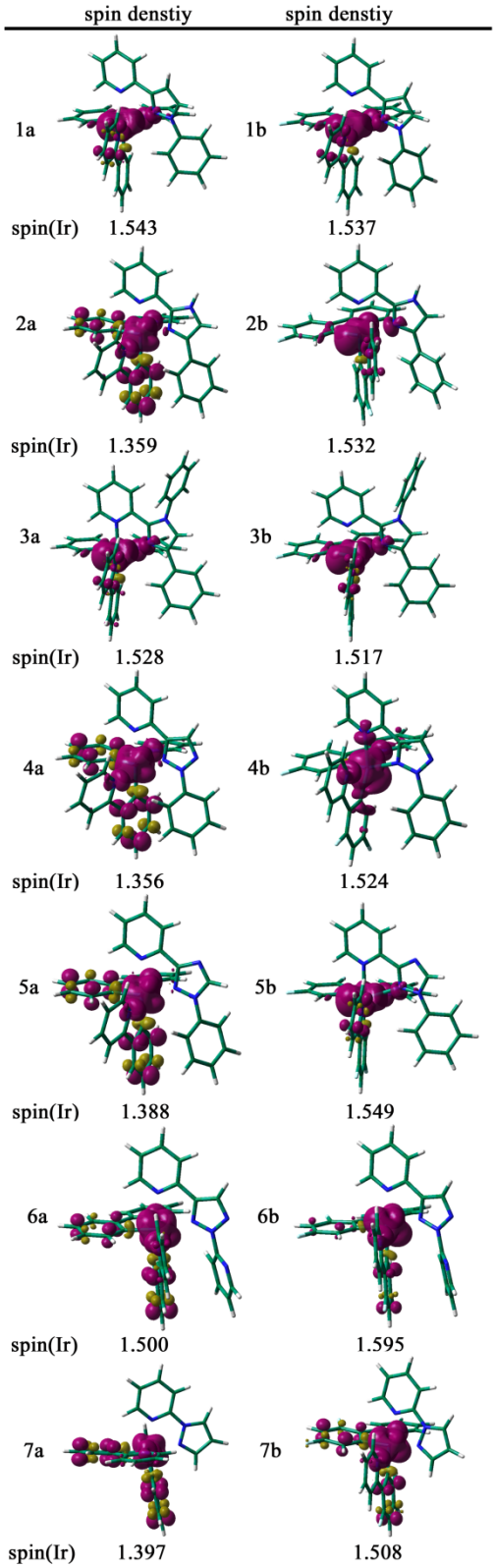

Fig. S1. Spin density distribution (0.003 e bohr^{-3}) and net spin value located on iridium(III) center calculated for the ^{3}MC excited states of **1a-7a** and **1b-7b**.

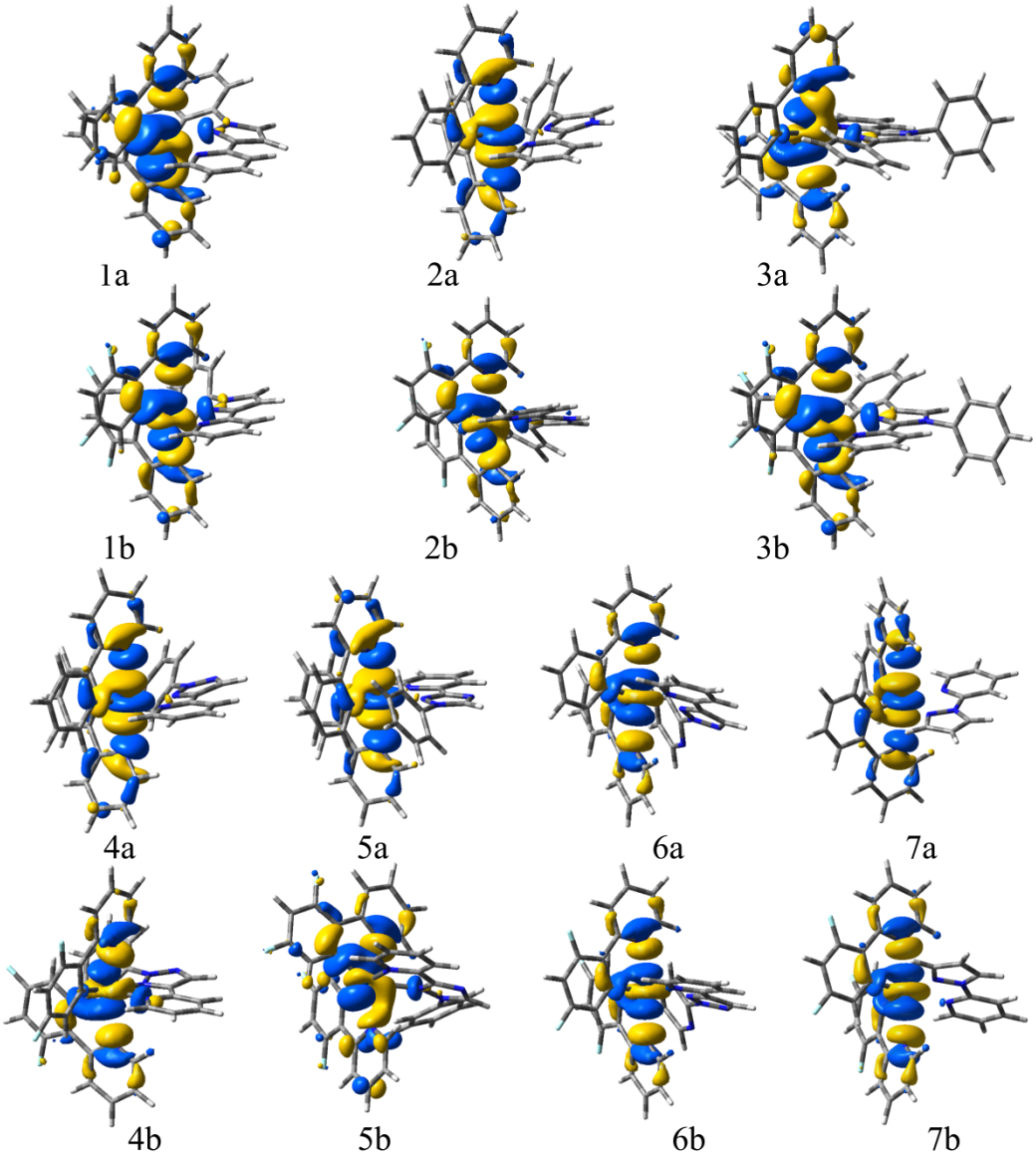

Fig. S2. electron density contours (0.035 e Bohr^{-3}) calculated for the unoccupied e_g molecular orbital of **1a-7a** and **1b-7b**. showing σ-antibonding interactions along the vertical N_{ppy}-Ir-N_{ppy} axis.