

Supporting information

DFT/TDDFT Study on the Electronic Structures and Optoelectronic Properties of Several Red-Emitting Osmium(II) Complexes with different P[^]P Ancillary Ligands

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Table S1. Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **1**.

MO	Energy/eV	Composition				assign
		Os	P [^] P	N [^] N ₁	N [^] N ₂	
L+9	1.64	23.8	49.6	4.5	4.8	d*(Os)+π*(P [^] P)
L+8	1.60	1.6	13.7	-2.4	-2.7	π*(P [^] P)
L+7	1.27	10.7	59.5	6.9	6.9	d*(Os)+π*(P [^] P)
L+6	1.07	10.0	28.1	0.8	0.8	d*(Os)+π*(P [^] P)
L+5	0.46	1.1	0.9	48.4	49.3	π*(N [^] N)
L+4	0.42	0.4	1.5	49.2	48.3	π*(N [^] N)
L+3	-0.50	1.2	1.1	48.3	48.8	π*(N [^] N)
L+2	-0.57	0.0	0.1	49.8	49.3	π*(N [^] N)
L+1	-1.46	5.5	1.7	45.9	46.1	π*(N [^] N)
L	-1.65	0.8	0.7	48.9	48.7	π*(N [^] N)
Gap				3.34		
H	-4.99	67.1	3.5	14.5	14.5	d(Os)+π(N [^] N)
H-1	-5.32	52.2	8.1	19.1	19.1	d(Os)+π(N [^] N)
H-2	-5.41	62.4	9.2	14.5	14.5	d(Os)+π(N [^] N)
H-3	-6.10	13.3	2.0	41.9	42.4	d(Os)+π(N [^] N)
H-4	-6.17	12.3	1.5	43.5	42.9	d(Os)+π(N [^] N)
H-5	-6.98	2.1	0.4	47.9	49.5	π(N [^] N)
H-6	-7.02	1.9	1.1	49.2	47.8	π(N [^] N)
H-7	-7.21	0.3	2.5	11.5	85.4	π(N [^] N)
H-8	-7.21	0.3	2.7	85.3	11.3	π(N [^] N)
H-9	-7.48	3.3	22.9	36.2	36.4	π(N [^] N/P [^] P)

Table S2. Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **2**.

MO	Energy/eV	Composition				Assign
		Os	P [^] P	N [^] N ₁	N [^] N ₂	
L+9	1.67	10.5	9.7	0.1	0.1	d*(Os)+π*(P [^] P)
L+8	1.51	7.3	14.3	9.8	9.8	π*(P [^] P/N [^] N)
L+7	1.25	23.1	24.9	3.9	3.9	d*(Os)+π*(P [^] P)
L+6	0.41	1.1	0.7	48.9	48.9	π*(N [^] N)
L+5	0.37	0.8	0.9	48.9	48.9	π*(N [^] N)
L+4	-0.53	0.1	95.6	2.2	2.2	π*(P [^] P)
L+3	-0.58	0.9	5.3	46.6	46.6	π*(N [^] N)
L+2	-0.65	0.1	0.3	49.5	49.5	π*(N [^] N)
L+1	-1.55	4.8	1.6	46.4	46.4	π*(N [^] N)
L	-1.70	1.1	0.7	48.7	48.7	π*(N [^] N)
Gap				3.35		
H	-5.05	65.3	4.2	15.1	15.1	d(Os)+π(N [^] N)
H-1	-5.27	57.7	6.5	17.1	17.1	d(Os)+π(N [^] N)
H-2	-5.63	58.6	9.3	16.0	16.0	d(Os)+π(N [^] N)
H-3	-6.12	11.3	1.3	43.5	43.5	d(Os)+π(N [^] N)
H-4	-6.24	15.8	2.3	40.9	40.9	d(Os)+π(N [^] N)
H-5	-7.02	2.1	0.5	48.6	48.7	π(N [^] N)
H-6	-7.06	1.6	1.1	48.6	48.6	π(N [^] N)
H-7	-7.21	0.4	3.4	47.8	47.8	π(N [^] N)
H-8	-7.22	0.2	2.1	48.7	48.7	π(N [^] N)
H-9	-7.53	3.4	21.1	37.0	37.0	π(N [^] N/P [^] P)

Table S3. Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **3**.

MO	Energy/eV	Composition				Assign
		Os	P [^] P	N [^] N ₁	N [^] N ₂	
L+9	1.56	6.4	11.7	9.9	9.9	$\pi^*(P^{\wedge}P/N^{\wedge}N)$
L+8	1.29	23.9	28.2	4.3	4.3	$d^*(Os)+\pi^*(P^{\wedge}P)$
L+7	0.42	1.1	0.7	48.9	48.9	$\pi^*(N^{\wedge}N)$
L+6	0.38	0.8	1.0	48.8	48.8	$\pi^*(N^{\wedge}N)$
L+5	-0.48	1.3	97.2	1.0	1.0	$\pi^*(P^{\wedge}P)$
L+4	-0.56	0.2	79.6	10.1	10.1	$\pi^*(P^{\wedge}P)$
L+3	-0.58	0.8	21.3	38.7	38.7	$\pi^*(N^{\wedge}N/P^{\wedge}P)$
L+2	-0.64	0.1	1.4	48.9	48.9	$\pi^*(N^{\wedge}N)$
L+1	-1.54	4.8	1.5	46.4	46.4	$\pi^*(N^{\wedge}N)$
L	-1.70	1.1	0.9	48.7	48.7	$\pi^*(N^{\wedge}N)$
Gap				3.34		
H	-5.04	65.3	4.4	15.0	15.0	$d(Os)+\pi(N^{\wedge}N)$
H-1	-5.25	57.6	7.0	16.9	16.9	$d(Os)+\pi(N^{\wedge}N)$
H-2	-5.61	59.2	9.6	15.6	15.6	$d(Os)+\pi(N^{\wedge}N)$
H-3	-6.11	11.1	1.3	43.6	43.6	$d(Os)+\pi(N^{\wedge}N)$
H-4	-6.23	15.2	2.4	41.1	41.1	$d(Os)+\pi(N^{\wedge}N)$
H-5	-7.01	2.0	0.6	48.6	48.6	$\pi(N^{\wedge}N)$
H-6	-7.05	1.5	1.4	48.5	48.5	$\pi(N^{\wedge}N)$
H-7	-7.19	0.4	8.0	45.5	45.5	$\pi(N^{\wedge}N)$
H-8	-7.20	0.2	2.3	48.6	48.6	$\pi(N^{\wedge}N)$
H-9	-7.36	0.1	93.7	3.1	3.1	$\pi(P^{\wedge}P)$

Table S4. Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **4**.

MO	Energy/eV	Composition				Assign
		Os	P [^] P	N [^] N ₁	N [^] N ₂	
L+9	1.30	24.0	28.6	4.3	4.3	d*(Os)+π*(P [^] P)
L+8	0.68	0.7	97.6	0.8	0.8	π*(P [^] P)
L+7	0.42	1.1	0.7	48.9	48.9	π*(N [^] N)
L+6	0.38	0.7	1.8	48.5	48.5	π*(N [^] N)
L+5	-0.57	0.9	3.7	47.4	47.4	π*(N [^] N)
L+4	-0.61	0.1	97.2	1.3	1.3	π*(P [^] P)
L+3	-0.64	0.1	0.4	49.4	49.4	π*(N [^] N)
L+2	-1.37	1.2	97.2	1.0	1.0	π*(P [^] P)
L+1	-1.54	4.8	1.4	46.4	46.4	π*(N [^] N)
L	-1.70	0.9	2.6	47.9	47.9	π*(N [^] N)
Gap				3.34		
H	-5.04	65.3	4.6	14.9	14.9	d(Os)+π(N [^] N)
H-1	-5.25	57.5	7.3	16.8	16.8	d(Os)+π(N [^] N)
H-2	-5.61	59.3	9.6	15.5	15.5	d(Os)+π(N [^] N)
H-3	-6.11	11.0	1.3	43.7	43.6	d(Os)+π(N [^] N)
H-4	-6.22	14.5	5.4	40.0	40.0	d(Os)+π(N [^] N)
H-5	-6.36	0.8	96.6	1.3	1.3	π(P [^] P)
H-6	-7.01	2.1	0.6	48.6	48.6	π(N [^] N)
H-7	-7.05	1.5	3.0	47.7	47.7	π(N [^] N)
H-8	-7.12	0.1	82.5	8.6	8.6	π(P [^] P)
H-9	-7.20	0.2	2.1	49.0	48.3	π(N [^] N)

Table S5. Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **5**.

MO	Energy/eV	Composition				Assign
		Os	P [^] P	N [^] N ₁	N [^] N ₂	
L+9	1.05	24.7	35.1	4.6	5.0	d*(Os)+π*(P [^] P)
L+8	1.03	2.3	94.8	1.0	0.3	π*(P [^] P)
L+7	0.26	1.0	0.8	38.1	59.7	π*(N [^] N)
L+6	0.22	0.9	1.1	59.5	38.0	π*(N [^] N)
L+5	-0.74	0.9	1.2	41.1	56.3	π*(N [^] N)
L+4	-0.80	0.1	0.8	56.7	41.7	π*(N [^] N)
L+3	-1.02	1.0	98.3	0.5	0.5	π*(P [^] P)
L+2	-1.67	0.7	93.7	4.9	0.7	π*(P [^] P)
L+1	-1.72	4.3	6.1	39.6	49.1	π*(N [^] N)
L	-1.88	0.9	2.3	50.8	45.3	π*(N [^] N)
Gap				3.42		
H	-5.30	64.1	4.4	15.3	15.8	d(Os)+π(N [^] N)
H-1	-5.49	55.2	7.2	18.2	17.7	d(Os)+π(N [^] N)
H-2	-5.87	56.4	9.3	17.0	17.2	d(Os)+π(N [^] N)
H-3	-6.30	12.4	1.5	42.1	43.6	d(Os)+π(N [^] N)
H-4	-6.43	17.8	2.8	40.5	38.9	d(Os)+π(N [^] N)
H-5	-7.18	2.3	0.6	44.5	52.5	d(Os)+π(N [^] N)
H-6	-7.22	1.6	0.9	52.7	44.7	π(N [^] N)
H-7	-7.38	0.4	3.3	79.7	16.1	π(N [^] N)
H-8	-7.39	0.2	2.3	16.9	80.2	π(N [^] N)
H-9	-7.68	0.1	97.0	1.3	1.6	π(P [^] P)

Table S6. Selected calculated wavelength (nm) /energies (eV), oscillator strength (f), major contribution, and transition characters of complexes **1-5**.

	State	λ/E	Oscillator	Configuration	Nature	Exptl ^[23]
1	S ₁	523/2.37	0.0155	H→L(69%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₄	433/2.86	0.0819	H-2→L(55%)	MLCT/LLCT[d(Os)+π(P [^] P)→π*(N [^] N)]	
				H-1→L+1(41%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
				H-1→L+1(55%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₅	423/2.93	0.1807	H-1→L+1(55%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₆	387/3.20	0.1625	H-2→L+1(65%)	MLCT/LLCT[d(Os)+π(P [^] P)→π*(N [^] N)]	
	S ₁₀	326/3.80	0.1281	H-4→L(59%)	ILCT/MLCT[π(N [^] N)+d(Os)→π*(N [^] N)]	
	S ₁₄	307/4.03	0.0752	H-1→L+3(65%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₁₅	304/4.08	0.2543	H-1→L+2(52%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₁₆	297/4.18	0.3135	H-2→L+3(60%)	MLCT/IL/LLCT[d(Os)+π(N [^] N)+π(P [^] P)→π*(N [^] N)]	
	S ₂₃	263/4.72	0.0741	H-3→L+2(45%)	ILCT/MLCT[π(N [^] N)+d(Os)→π*(N [^] N)]	
	S ₄₂	235/5.27	0.1266	H-9→L+1(45%)	LLCT/LM/ILC[π(P [^] P)+π(N [^] N)→d(Os)+π*(N [^] N)]	
	S ₄₃	233/5.33	0.1427	H-13→L(37%)	ILCT[π(N [^] N)→π*(N [^] N)]	
	S ₄₅	232/5.34	0.1164	H-12→L(45%)	ILCT/LLCT[π(N [^] N)+π(P [^] P)→π*(N [^] N)]	
	S ₅₇	217/5.71	0.2250	H-3→L+4(42%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₅₈	216/5.74	0.1564	H-15→L(36%)	ILCT/MLCT[π(N [^] N+d(Os))→π*(N [^] N)]	
				H-3→L+5(36%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
				H-4→L+5(31%)	ILCT/MLCT [π(N [^] N +d(Os))→π*(N [^] N)]	
2	S ₁	512/2.42	0.0238	H→L(69%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₅	404/3.07	0.2015	H-2→L(68%)	MLCT[d(Os)→π*(N [^] N)]	
	S ₆	373/3.32	0.1337	H-2→L+1(66%)	MLCT[d(Os)→π*(N [^] N)]	
	S ₁₁	324/3.83	0.1823	H-4→L(61%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₁₇	294/4.21	0.2475	H-2→L+2(65%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₁₉	288/4.31	0.2634	H-2→L+3(63%)	MLCT/ ILCT [d(Os) +π(N [^] N) →π*(N [^] N)]	
	S ₄₅	234/5.30	0.1324	H-2→L+5(37%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₄₇	233/5.33	0.1038	H-12→L(34%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₄₈	233/5.33	0.1280	H-11→L(35%)	LLCT[π(P [^] P)→π*(N [^] N)]	
	S ₅₇	221/5.61	0.1956	H-16→L(33%)	LLCT/ILCT[π(P [^] P)+π(N [^] N) →π*(N [^] N)]	
	S ₅₉	218/5.69	0.0755	H-16→L+1(38%)	LLCT/LMCT[π(P [^] P)+π(N [^] N)→π*(N [^] N)+d(Os)]	
				H-14→L+1(36%)	LLCT/ILCT[π(P [^] P)+π(N [^] N)→π*(N [^] N)]	
				H-15→L(43%)	LLCT/ILCT[π(P [^] P)+π(N [^] N)→π*(N [^] N)]	
	S ₆₀	217/5.72	0.1365	H-3→L+5(37%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
3	S ₁	511/2.43	0.0229	H→L(69%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₅	404/3.07	0.1985	H-2→L(68%)	MLCT[d(Os)→π*(N [^] N)]	418
	S ₆	374/3.32	0.1634	H-2→L+1(66%)	MLCT[d(Os)→π*(N [^] N)]	356
	S ₁₀	324/3.82	0.1765	H-4→L(61%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	342
	S ₁₈	294/4.21	0.2446	H-2→L+2(65%)	MLCT/ ILCT [d(Os) +π(N [^] N) →π*(N [^] N)]	
	S ₁₉	294/4.22	0.1003	H-1→L+5(68%)	MLCT/LLCT[d(Os)+π(N [^] N)→π*(P [^] P)]	
	S ₂₀	288/4.31	0.2463	H-2→L+3(63%)	MLCT/ ILCT [d(Os) +π(N [^] N) →π*(N [^] N)]	307
	S ₂₈	263/4.71	0.0933	H-3→L+2(39%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
				H→L+7(32%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
				H-2→L+6(31%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₅₃	234/5.30	0.1944	H-13→L(28%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
				H-12→L(28%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
				H-11→L(21%)	LLCT/MLCT[π(P [^] P)+d(Os)→π*(N [^] N)]	
S ₅₄	233/5.32	0.1745	H-11→L(21%)	LLCT[π(P [^] P)→π*(N [^] N)]		
4	S ₁	511/2.43	0.0223	H→L(69%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]	
	S ₅	404/3.07	0.1970	H-2→L(68%)	MLCT[d(Os)→π*(N [^] N)]	

	S ₇	375/3.31	0.2387	H-2→L+1(63%)	MLCT[d(Os)→π*(N [^] N)]
	S ₁₃	325/3.82	0.1770	H-5→L(56%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
	S ₂₂	294/4.22	0.2439	H-2→L+3(65%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
	S ₂₃	288/4.31	0.3683	H-2→L+4(64%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
	S ₃₄	263/4.71	0.1294	H-3→L+3(38%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
				H→L+7(35%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
	S ₄₆	248/5.01	0.1115	H-1→L+6(40%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
				H-1→L+9(31%)	MC(d-d)/IL/LLCT[π(N [^] N)→π*(N [^] N)+π*(P [^] P)]
	S ₅₉	234/5.31	0.1342	H-2→L+6(33%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
				H→L+7(28%)	MLCT/LLCT[d(Os)+π(N [^] N)→π*(P [^] P)]
				H-2→L+9(24%)	MLCT[d(Os)→π*(P [^] P)]
	S ₆₀	233/5.31	0.3717	H-12→L(27%)	LLCT/ILCT[π(P [^] P)+π(N [^] N)→π*(N [^] N)]
				H-2→L+7(26%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
5	S ₁	494/2.51	0.0254	H→L(69%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
	S ₇	393/3.15	0.1922	H-2→L(67%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
	S ₈	365/3.39	0.1564	H-2→L+1(66%)	MLCT[d(Os)→π*(N [^] N)]
	S ₁₄	323/3.83	0.1909	H-4→L(62%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
	S ₂₃	288/4.30	0.2334	H-2→L+4(66%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
	S ₂₄	283/4.38	0.3044	H-2→L+5(64%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
	S ₅₂	235/5.27	0.0703	H-7→L+2(60%)	LLCT[π(N [^] N)→π*(P [^] P)]
	S ₅₄	233/5.31	0.2069	H-10→L(41%)	LLCT/ILCT[π(P [^] P)+π(N [^] N)→π*(N [^] N)]
	S ₅₅	233/5.32	0.0824	H-1→L+17(30%)	LMCT[π*(N [^] N)→d(Os)]
				H-1→L+13(25%)	MLCT[d(Os)→π*(N [^] N)]
				H-1→L+11(22%)	MLCT/LLCT[d(Os)+π(N [^] N)→π*(P [^] P)]
	S ₅₆	233/5.33	0.1455	H-12→L(29%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]
				H-8→L+2(25%)	LLCT[π(N [^] N)→π*(P [^] P)]
				H-5→L+4(20%)	ILCT[π(N [^] N)→π*(N [^] N)]
	S ₅₈	231/5.36	0.2027	H-2→L+7(55%)	MLCT/ILCT[d(Os)+π(N [^] N)→π*(N [^] N)]