Supporting Information

Are Re(I) Phenanthroline Complexes Suitable Candidates for OLEDs?

Answers from DFT and TD-DFT Investigations

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Table S1. The optimized ground state geometries of complex **1** obtained using different functional with LANL2DZ[#] basis set along with the experimental data.

	PBE1PBE	B3LYP	B3P86	BPBE	BPW91	Exp*
Bond length (Å)						
Re-C1	1.915	1.926	1.916	1.922	1.923	1.917
Re-C2	1.915	1.926	1.916	1.922	1.923	1.915
Re-C3	1.962	1.976	1.964	1.971	1.972	1.952
Re-C4	2.144	2.168	2.147	2.159	2.161	2.144
Re-N1	2.182	2.214	2.184	2.194	2.197	2.165
Re-N2	2.182	2.214	2.184	2.194	2.197	2.177
Bond angle (°)						
C1-Re-C2	90.45	90.95	90.59	90.67	90.70	90.21
N1-Re-N2	75.42	74.95	75.44	75.50	75.43	75.77

* X-ray crystal diffraction data (ref. 29)

LANL2DZ for Re atom, 6-31g(d) for all other atoms

Table S2. The optimized ground state geometries of complex **1** obtained using PBE1PBE functional with different basis sets along with the experimental data.

	LANL2DZ/6-31G(d)	LANL2DZ /6-311G(d)	LANL2DZ /6-311+G(d)	Exp*
Bond length (Å)				
Re-C1	1.915	1.915	1.917	1.917
Re-C2	1.915	1.915	1.917	1.915
Re-C3	1.962	1.965	1.961	1.952
Re-C4	2.144	2.146	2.158	2.144
Re-N1	2.182	2.184	2.185	2.165
Re-N2	2.182	2.184	2.185	2.177
Bond angle (°)				
C1-Re-C2	90.45	89.83	89.44	90.21
N1-Re-N2	75.42	75.21	75.17	75.77

* X-ray crystal diffraction data (ref. 29)

Table S3. The calculated lowest-lying transitions of complex **1** obtained using different functional with LANL2DZ[#] basis set.

	PBE1PBE	B3LYP	B3P86	BPBE	BPW91	M06	M06-2X
Peak 1	422 (2.94)	442 (2.81)	439 (2.82)	571 (2.17)	572 (2.17)	426 (2.91)	326 (3.80)
	M05	M05-2X	TPSSLYP1W	wB97XD	M11	M11-L	Exp*/nm (eV)
Peak 1	428 (2.89)	323 (3.83)	531 (2.33)	336 (3.69)	295 (4.19)	507 (2.44)	380 (3.26)

* ref. 29

LANL2DZ for Re atom, 6-31g(d) for all other atoms

Table S4. TD-DFT calculation on the lowest-lying absorption of complex **1** using PBE1PBE functional with different basis sets.

	LANL2DZ /6-31G(d)	LANL2DZ /6-311G(d)	LANL2DZ /6-311+G(d)
Peak 1	422	425	423

Table S5. Calculated and experimental emission energies of complex **1**.

	$\Delta E_{T_1-S_0}$ (eV)/(nm)	CIS/nm	TD-DFT/nm	Exp*/nm
λ_{em}	2.23/556	585	591	602

* ref. 29

$\Delta E_{T_1-S_0}$ is the energy difference between the ground singlet and triplet.

Table S6. Frontier molecular orbital compositions (%) in the ground state for complex **1** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	CO	Phen	benzoxazole	
L+5	-0.182	20.37	57.69	11.99	9.95	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+4	-0.219	1.78	5.02	92.63	0.58	π*(phen)
L+3	-0.563	23.18	32.89	30.99	12.95	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+2	-1.020	2.82	1.83	93.63	1.72	π*(phen)
L+1	-2.349	0.18	0.53	99.25	0.05	π*(phen)
L	-2.412	4.26	4.17	88.80	2.68	π*(phen)
H	-5.500	22.19	10.73	2.68	64.41	d(Re) + π(CO) + π(benzoxazole)
H-1	-6.150	1.69	0.66	1.17	96.47	d(Re) + π(benzoxazole)
H-2	-6.311	62.66	23.59	10.98	2.77	d(Re) + π(CO) + π(phen)
H-3	-6.491	67.00	27.89	3.06	2.05	d(Re) + π(CO)
H-4	-6.546	47.53	18.52	7.23	26.72	d(Re) + π(CO) + π(benzoxazole)
H-5	-6.969	5.06	3.53	7.67	83.75	π(benzoxazole)

Table S7. Frontier molecular orbital compositions (%) in the ground state for complex **2** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	CO	phen	benzoxazole	
L+5	-3.075	21.35	51.02	12.92	14.71	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+4	-3.212	11.16	28.79	17.04	43.01	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+3	-3.823	3.48	2.84	90.56	3.12	π*(phen)
L+2	-4.342	16.33	20.75	12.15	50.77	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+1	-5.096	0.06	0.50	99.34	0.10	π*(phen)
L	-5.290	4.79	4.23	88.03	2.95	π*(phen)
H	-9.362	49.22	17.53	4.77	28.48	d(Re) + π(CO) + π(benzoxazole)
H-1	-9.626	59.13	20.64	17.13	3.09	d(Re) + π(CO) + π(phen)
H-2	-9.769	68.95	27.61	2.95	0.49	d(Re) + π(CO)
H-3	-10.263	0.95	0.64	0.57	97.84	π(benzoxazole)
H-4	-10.379	14.55	5.99	14.40	65.07	d(Re) + π(phen) + π(benzoxazole)
H-5	-10.380	11.09	3.96	82.12	2.83	d(Re) + π(phen)

Table S8. Frontier molecular orbital compositions (%) in the ground state for complex **3** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	CO	phen	benzoxazole	
L+5	-3.083	0.24	3.77	94.15	1.83	π*(phen)
L+4	-3.488	27.55	40.08	26.45	5.92	p(Re) + π*(CO) + π*(phen)
L+3	-3.840	3.14	2.29	90.27	4.31	π*(phen)
L+2	-4.077	11.61	14.92	10.04	63.43	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+1	-5.118	0.29	0.63	97.70	1.38	π*(phen)
L	-5.316	4.53	3.94	88.56	2.98	π*(phen)
H	-9.303	47.20	16.21	8.25	28.34	d(Re) + π(CO) + π(benzoxazole)
H-1	-9.502	65.66	23.74	7.75	2.85	d(Re) + π(CO)
H-2	-9.679	68.90	27.45	3.02	0.64	d(Re) + π(CO)
H-3	-10.150	2.53	1.08	7.90	88.49	π(benzoxazole)
H-4	-10.190	3.60	2.18	39.21	55.02	π(phen) + π(benzoxazole)
H-5	-10.492	17.76	6.18	51.36	24.70	d(Re) + π(phen) + π(benzoxazole)

Table S9. Frontier molecular orbital compositions (%) in the ground state for complex **4** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)					Main bond type
		Re	CO	phen	benzoxazole	PPh_3	
L+5	-2.828	10.53	0.91	12.39	5.51	70.65	p(Re) + π*(phen) + π*(PPh_3)
L+4	-2.924	0.88	2.61	41.99	0.93	53.59	π*(phen) + π*(PPh_3)
L+3	-3.480	12.98	8.47	15.14	46.29	17.11	p(Re) + π*(benzoxazole) + π*(phen) + π*(PPh_3)
L+2	-3.522	4.70	2.25	81.31	6.47	5.27	π*(phen)
L+1	-4.807	0.45	0.47	97.87	0.25	0.97	π*(phen)
L	-4.962	6.39	2.21	84.30	3.63	3.47	π*(phen)
H	-8.371	53.26	12.25	4.03	25.05	5.42	d(Re) + π(CO) + π(benzoxazole)
H-1	-8.532	62.28	10.81	11.58	6.02	9.32	d(Re) + π(CO) + π(phen)
H-2	-8.933	65.77	27.18	3.35	0.76	2.93	d(Re) + π(CO)
H-3	-9.062	0.78	0.34	0.50	0.27	98.11	π(PPh_3)
H-4	-9.191	6.44	2.07	0.79	2.66	88.04	π(PPh_3)
H-5	-9.304	8.75	2.42	0.64	4.81	83.38	π(PPh_3)

Table S10. Frontier molecular orbital compositions (%) in the ground state for complex **5** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)					Main bond type
		Re	CO	phen	benzoxazole	PPh_2Me	
L+5	-2.667	6.72	4.21	21.63	20.64	46.80	π*(benzoxazole) + π*(phen) + π*(PPh_2Me)
L+4	-2.797	7.69	2.09	22.90	1.37	65.95	π*(phen) + π*(PPh_2Me)
L+3	-3.417	3.99	1.89	86.86	3.25	4.01	π*(phen)
L+2	-3.549	13.11	10.36	11.56	52.09	12.88	p(Re)+π*(CO)+π*(benzoxazole)+π*(phen)+π*(PPh_2Me)
L+1	-4.699	0.38	0.54	98.03	0.28	0.78	π*(phen)
L	-4.853	5.78	2.12	85.34	3.57	3.19	π*(phen)
H	-8.424	54.06	12.63	3.87	25.01	4.44	d(Re) + π(CO) + π(benzoxazole)
H-1	-8.653	63.62	12.63	10.89	5.49	7.37	d(Re) + π(CO) + π(phen)
H-2	-9.021	64.92	27.71	3.20	0.69	3.48	d(Re) + π(CO)
H-3	-9.156	6.65	2.00	0.71	2.61	88.03	π(PPh_2Me)
H-4	-9.322	1.12	0.81	0.21	0.98	96.88	π(PPh_2Me)
H-5	-9.568	6.45	1.58	3.16	4.17	84.65	π(PPh_2Me)

Table S11. Frontier molecular orbital compositions (%) in the ground state for complex **6** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)					Main bond type
		Re	CO	Phen	benzoxazole	$P(OEt)_3$	
L+5	-2.650	3.95	10.87	71.27	13.44	0.48	π*(CO) + π*(benzoxazole) + π*(phen)
L+4	-2.709	8.48	21.92	41.90	24.51	3.19	π*(CO) + π*(benzoxazole) + π*(phen)
L+3	-3.459	4.54	2.01	88.42	2.45	2.58	π*(phen)
L+2	-3.651	16.80	10.20	12.58	55.54	4.89	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+1	-4.734	0.41	0.54	97.55	0.28	1.21	π*(phen)
L	-4.878	5.09	2.28	86.20	4.13	2.30	π*(phen)
H	-8.609	53.86	11.69	4.58	25.35	4.52	d(Re) + π(CO) + π(benzoxazole)
H-1	-8.917	64.79	14.09	12.22	4.14	4.76	d(Re) + π(CO) + π(phen)
H-2	-9.165	66.94	28.68	3.16	0.53	0.68	d(Re) + π(CO)
H-3	-9.829	2.15	1.05	4.66	90.02	2.12	π(benzoxazole)
H-4	-9.872	8.76	2.45	49.11	17.43	22.24	d(Re) + π(phen) + π(benzoxazole) + π($P(OEt)_3$)
H-5	-9.928	11.29	3.88	12.01	70.77	2.04	d(Re) + π(phen) + π(benzoxazole)

Table S12. Frontier molecular orbital compositions (%) in the ground state for complex **7** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	CO	phen	RCN	
L+5	-3.179	13.07	31.59	18.72	36.62	p(Re) + π*(CO) + π*(RCN) + π*(phen)
L+4	-3.570	21.10	35.26	15.35	28.29	p(Re) + π*(CO) + π*(RCN) + π*(phen)
L+3	-3.878	2.69	2.47	93.83	1.01	π*(phen)
L+2	-4.282	18.08	23.56	13.13	45.23	p(Re) + π*(CO) + π*(RCN) + π*(phen)
L+1	-5.164	0.08	0.50	99.41	0.01	π*(phen)
L	-5.351	4.46	3.92	89.18	2.43	π*(phen)
H	-9.101	17.77	6.84	1.56	73.82	d(Re) + π(RCN)
H-1	-9.644	30.50	10.35	3.59	55.56	d(Re) + π(CO) + π(RCN)
H-2	-9.725	56.72	18.77	16.80	7.72	d(Re) + π(CO) + π(phen)
H-3	-9.821	69.18	26.48	3.88	0.46	d(Re) + π(CO)
H-4	-10.308	22.44	7.83	9.36	60.38	d(Re) + π(RCN)
H-5	-10.468	10.80	3.41	83.38	2.42	d(Re) + π(phen)

Table S13. Frontier molecular orbital compositions (%) in the excited state for complex **1** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	CO	phen	benzoxazole	
L+5	-0.342	3.71	24.93	8.44	62.92	π*(CO) + π*(benzoxazole) + π*(phen)
L+4	-0.500	16.75	61.00	10.55	11.69	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+3	-0.906	1.44	2.02	94.65	1.90	π*(phen)
L+2	-1.148	20.47	34.96	22.95	21.63	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+1	-2.298	2.15	4.09	90.34	3.43	π*(phen)
L	-2.522	0.03	0.37	99.58	0.02	π*(phen)
H	-6.231	41.76	19.60	2.87	35.77	d(Re) + π(CO) + π(benzoxazole)
H-1	-6.571	50.40	22.09	23.22	4.29	d(Re) + π(CO) + π(phen)
H-2	-6.764	64.87	29.54	2.83	2.76	d(Re) + π(CO)
H-3	-7.003	4.70	1.67	2.76	90.88	π(benzoxazole)
H-4	-7.116	13.00	6.16	63.33	17.50	d(Re) + π(phen) + π(benzoxazole)
H-5	-7.191	17.22	7.68	5.58	69.52	d(Re) + π(benzoxazole)

Table S14. Frontier molecular orbital compositions (%) in the excited state for complex **2** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	CO	phen	benzoxazole	
L+5	-0.878	16.70	54.49	17.29	11.51	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+4	-0.924	10.51	33.43	11.69	44.37	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+3	-1.109	3.17	6.08	85.83	4.91	π*(phen)+ π*(CO)
L+2	-1.924	13.72	21.87	13.62	50.79	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+1	-2.562	2.36	4.55	89.53	3.56	π*(phen)
L	-2.703	0.01	0.37	99.57	0.05	π*(phen)
H	-6.860	53.77	21.26	5.63	19.35	d(Re) + π(CO) + π(benzoxazole)
H-1	-6.951	42.64	17.42	36.70	3.24	d(Re) + π(CO) + π(phen)
H-2	-7.149	66.60	29.09	2.95	1.36	d(Re) + π(CO)
H-3	-7.428	25.37	9.19	63.85	1.58	d(Re) + π(CO) + π(phen)
H-4	-7.884	1.07	0.61	0.41	97.91	π(benzoxazole)
H-5	-8.031	5.43	2.36	14.99	77.23	d(Re) + π(phen)+ π(benzoxazole)

Table S15. Frontier molecular orbital compositions (%) in the excited state for complex **3** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	CO	phen	benzoxazole	
L+5	-0.697	11.83	42.66	8.51	37.00	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+4	-1.119	2.32	4.14	91.08	2.47	π*(phen)
L+3	-1.263	24.81	48.48	21.97	4.73	p(Re) + π*(CO) + π*(benzoxazole)
L+2	-1.708	9.28	15.72	8.75	66.25	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+1	-2.578	2.22	4.18	90.29	3.31	π*(phen)
L	-2.725	0.15	0.60	98.52	0.73	π*(phen)
H	-6.829	45.68	17.99	19.99	16.34	d(Re) + π(CO) + π(phen)+ π(benzoxazole)
H-1	-6.967	62.31	25.20	8.91	3.58	d(Re) + π(CO) + π(phen)
H-2	-7.130	66.80	29.34	3.38	0.48	d(Re) + π(CO)
H-3	-7.364	8.36	3.11	77.15	11.37	π(phen)
H-4	-7.832	1.14	0.44	0.46	97.96	d(Re) + π(benzoxazole)
H-5	-8.050	11.13	4.37	5.17	79.33	d(Re) + π(phen)+ π(benzoxazole)

Table S16. Frontier molecular orbital compositions (%) in the excited state for complex **4** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)					Main bond type
		Re	CO	phen	benzoxazole	PPh_3	
L+5	-0.853	5.07	2.77	6.82	8.33	77.02	p(Re) + π*(phen) + π*(PPh_3)+ π*(benzoxazole)
L+4	-0.947	1.90	0.35	3.13	3.83	90.80	π*(PPh_3)
L+3	-1.027	1.61	1.65	82.99	2.93	10.83	π*(phen) + π*(PPh_3)
L+2	-1.510	7.56	8.09	10.05	50,24	24.06	p(Re)+π(CO)+ π*(phen)+ π*(benzoxazole)+ π(PPh_3)
L+1	-2.452	3.00	3.33	86.58	2.59	4.49	π*(phen)
L	-2.602	0.06	0.35	98.49	0.08	1.01	π*(phen)
H	-6.244	52.59	14.17	4.59	18.81	9.83	d(Re) + π(CO) + π(benzoxazole)+ π(PPh_3)
H-1	-6.379	55.84	14.06	12.28	6.50	11.31	d(Re) + π(CO) + π(phen)+ π(benzoxazole)+ π(PPh_3)
H-2	-6.772	63.15	30.54	3.67	1.53	1.11	d(Re) + π(CO)
H-3	-7.238	6.70	1.71	87.37	0.98	3.25	d(Re) + π(PPh_3)
H-4	7.316	7.12	2.06	0.74	9.13	80.95	d(Re) + π(benzoxazole)+ π(PPh_3)
H-5	-7.506	0.95	0.27	0.69	1.21	96.89	π(PPh_3)

Table S17. Frontier molecular orbital compositions (%) in the excited state for complex **5** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)					Main bond type
		Re	CO	phen	benzo xazole	PPh_2Me	
L+5	-0.723	6.43	2.29	3.42	9.13	78.73	p(Re) + π*(benzoxazole) + π*(PPh_2Me)
L+4	-0.816	1.08	0.28	3.48	3.85	91.31	π*(PPh_2Me)
L+3	-1.014	1.52	1.56	89.30	2.96	4.66	π*(phen)
L+2	-1.459	8.26	8.56	10.08	57.19	15.92	p(Re)+π*(CO)+π*(benzoxazole)+π*(phen)+π*(PPh_2Me)
L+1	-2.436	2.79	3.07	87.74	2.61	3.79	π*(phen)
L	-2.608	0.12	0.39	98.70	0.14	0.65	π*(phen)
H	-6.188	54.33	14.47	4.37	19.18	7.65	d(Re) + π(CO) + π(benzoxazole)+ π(PPh_2Me)
H-1	-6.340	57.16	14.61	11.88	6.12	10.24	d(Re) + π(CO) + π(phen) + π(PPh_2Me)
H-2	-6.718	63.74	30.84	3.09	1.49	0.85	d(Re) + π(CO)
H-3	-7.225	5.95	1.67	86.66	1.57	4.16	d(Re) + π(phen)
H-4	-7.330	5.01	1.29	1.69	7.10	84.91	π(benzoxazole) + π(PPh_2Me)
H-5	-7.627	0.90	0.24	2.66	1.12	95.08	π(PPh_2Me)

Table S18. Frontier molecular orbital compositions (%) in the excited state for complex **6** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)					Main bond type
		Re	CO	Phen	benzo xazole	$P(OEt)_3$	
L+5	-0.294	0.29	8.36	81.11	8.04	2.19	π*(CO) + π*(benzoxazole) + π*(phen)
L+4	-0.609	11.65	34.54	15.42	35.83	2.55	p(Re) + π*(CO) + π*(benzoxazole) + π*(phen)
L+3	-0.899	1.80	2.30	90.72	2.91	2.26	π*(phen)
L+2	-1.466	11.80	9.25	13.45	58.09	7.40	p(Re)+π*(CO)+π*(benzoxazole)+π*(phen)+ π*($P(OEt)_3$)
L+1	-2.339	2.65	3.36	87.00	2.71	4.28	π*(phen)
L	-2.490	0.07	0.37	99.20	0.10	0.25	π*(phen)
H	-6.348	55.43	13.40	5.65	20.44	5.08	d(Re) + π(CO) + π(benzoxazole)
H-1	-6.536	55.61	14.93	19.75	4.48	5.23	d(Re) + π(CO) + π(phen)
H-2	-6.800	64.76	30.68	2.93	1.26	0.36	d(Re) + π(CO)
H-3	-7.128	12.01	3.06	79.71	2.02	3.20	d(Re) + π(benzoxazole)
H-4	-7.667	1.02	0.56	0.46	97.83	0.14	π(benzoxazole)
H-5	-7.820	4.57	1.74	15.77	77.32	0.60	d(Re) + π(phen) + π(benzoxazole)

Table S19. Frontier molecular orbital compositions (%) in the excited state for complex **7** computed at the PBE1PBE/LANL2DZ level.

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	CO	phen	RCN	
L+5	-0.995	11.03	35.61	11.28	42.08	p(Re) + π*(CO) + π*(RCN) + π*(phen)
L+4	-1.091	2.03	3.39	92.50	2.08	π*(phen)
L+3	-1.254	19.61	43.24	13.78	23.36	p(Re) + π*(CO) + π*(RCN) + π*(phen)
L+2	-1.892	15.61	25.74	13.45	45.20	p(Re) + π*(CO) + π*(RCN) + π*(phen)
L+1	-2.574	2.53	4.65	90.02	2.80	π*(phen)
L	-2.679	0.01	0.42	99.55	0.01	π*(phen)
H	-6.832	26.31	10.65	2.83	60.20	d(Re)+ π(CO) + π(RCN)
H-1	-7.035	30.22	12.16	53.60	4.02	d(Re) + π(CO) + π(phen)
H-2	-7.246	29.25	10.97	4.52	55.26	d(Re) + π(CO) + π(RCN)
H-3	-7.265	67.52	28.72	3.34	0.42	d(Re) + π(CO)
H-4	-7.501	37.11	12.87	45.58	4.43	d(Re) + π(CO)+ π(phen)
H-5	-8.013	6.71	2.61	11.33	79.35	d(Re) + π(phen)+ π(RCN)

Table S20. Natural population (NPA) charges on selected atoms for complexes **1**-**7** computed at PBE1PBE/LANL2DZ[#] level.

Atom	1	2	3	4	5	6	7
Re	-1.084	-1.102	-1.097	-1.118	-1.139	-1.265	-1.167
C1	0.751	0.736	0.754	0.718	0.711	0.715	0.755
C2	0.751	0.736	0.728	0.728	0.707	0.716	0.755
C3	0.717	0.754	0.752	-	-	-	0.760
C4	0.426	0.536	0.539	0.550	0.550	0.545	0.507
N1	-0.356	-0.379	-0.378	-0.382	-0.374	-0.372	-0.377
N2	-0.356	-0.379	-0.379	-0.376	-0.375	-0.372	-0.377
P1	-	-	-	1.301	1.309	1.307	-

LANL2DZ for Re atom, 6-31g(d) for all other atoms

Table S21: Wiberg bond index, occupancies and natural hybrid orbital composition of the calculated natural bond orbitals (NBOs) for complexes **1-7** calculated at PBE1PBE/LANL2DZ[#] level.

Complex	Bond (X-Y)	WBI	Occupancy	Bond Orbital	EDX%	EDY%
1	Re-CO(1)	1.2979	1.96053	0.6211 ($s^{22.99\%}p^{16.85\%}d^{60.15\%}$) Re + 0.7837 ($s^{65.98\%}p^{34.01\%}d^{0.01\%}$) C	38.57	61.43
	Re-CO(2)	1.1997	1.92168	0.5625 ($s^{14.55\%}p^{48.60\%}d^{36.85\%}$) Re + 0.8268 ($s^{67.08\%}p^{32.91\%}d^{0.00\%}$) C	31.64	68.36
	Re-CO(3)	1.2978	1.96053	0.6211 ($s^{22.99\%}p^{16.85\%}d^{60.15\%}$) Re + 0.7837 ($s^{65.98\%}p^{34.01\%}d^{0.01\%}$) C	38.57	61.43
	Re-N1	0.4916	1.63936	0.9043 ($s^{0.04\%}p^{1.12\%}d^{98.84\%}$) Re + 0.4269 ($s^{0.06\%}p^{99.94\%}d^{0.00\%}$) N	81.77	18.23
	Re-C4	0.7525	1.85695	0.5644 ($s^{10.04\%}p^{49.29\%}d^{40.67\%}$) Re + 0.8255($s^{43.03\%}p^{56.97\%}d^{0.00\%}$) C	31.86	68.14
2	Re-CO(1)	1.2864	1.95508	0.6101 ($s^{25.64\%}p^{19.15\%}d^{55.21\%}$) Re + 0.7923 ($s^{66.48\%}p^{33.52\%}d^{0.00\%}$) C	37.23	62.77
	Re-CO(2)	1.2863	1.95610	0.6101 ($s^{25.52\%}p^{18.80\%}d^{55.67\%}$) Re + 0.7923 ($s^{65.94\%}p^{34.05\%}d^{0.00\%}$) C	37.23	62.77
	Re-CO(3)	1.1184	1.91343	0.5673 ($s^{14.39\%}p^{47.08\%}d^{38.52\%}$) Re + 0.8235 ($s^{66.72\%}p^{33.27\%}d^{0.00\%}$) C	32.19	67.81
	Re-N1	0.4961	1.73757	0.9359 ($s^{0.05\%}p^{0.37\%}d^{99.58\%}$) Re + 0.3522 ($s^{0.00\%}p^{99.88\%}d^{0.12\%}$) C	87.59	12.41
	Re-C4	0.7848	1.88419	0.5347 ($s^{11.02\%}p^{49.11\%}d^{39.87\%}$) Re + 0.8451 ($s^{48.48\%}p^{51.52\%}d^{0.00\%}$) C	28.59	71.41
3	Re-CO(1)	1.2586	1.95345	0.6097 ($s^{25.75\%}p^{18.59\%}d^{55.65\%}$) Re + 0.7926 ($s^{65.77\%}p^{34.22\%}d^{0.01\%}$) C	37.18	62.82
	Re-CO(2)	1.3015	1.95475	0.6088 ($s^{26.33\%}p^{18.85\%}d^{54.82\%}$) Re + 0.7934 ($s^{66.05\%}p^{33.95\%}d^{0.01\%}$) C	37.06	62.94
	Re-CO(3)	1.1405	1.91462	0.5653 ($s^{14.69\%}p^{48.20\%}d^{37.11\%}$) Re + 0.8249 ($s^{66.49\%}p^{33.51\%}d^{0.00\%}$) C	31.95	68.05
	Re-N1	0.4930	1.59048	0.9657 ($s^{0.10\%}p^{1.97\%}d^{97.93\%}$) Re + 0.2597 ($s^{0.97\%}p^{95.62\%}d^{3.41\%}$) N	93.25	6.75
	Re-C4	0.7640	1.88546 (σ)	0.5309 ($s^{11.51\%}p^{49.83\%}d^{38.66\%}$) Re + 0.8474 ($s^{48.48\%}p^{51.73\%}d^{0.00\%}$) C	28.18	71.82
4	Re-CO(1)	1.3341	1.96313	0.6255 ($s^{18.54\%}p^{17.32\%}d^{64.14\%}$) Re + 0.7802 ($s^{66.31\%}p^{33.68\%}d^{0.01\%}$) C	39.13	60.87
	Re-CO(2)	1.3294	1.96350	0.6278 ($s^{18.32\%}p^{16.94\%}d^{64.74\%}$) Re + 0.7784 ($s^{66.10\%}p^{33.89\%}d^{0.01\%}$) C	39.41	60.59
	Re-P	0.7332	1.90258	0.5905 ($s^{22.29\%}p^{25.15\%}d^{52.56\%}$) Re + 0.8070 ($s^{33.54\%}p^{66.40\%}d^{0.00\%}$) P	34.87	65.13
	Re-N1	0.5047	1.71017	0.9324 ($s^{0.50\%}p^{4.73\%}d^{94.77\%}$) Re + 0.3615 ($s^{0.37\%}p^{99.50\%}d^{0.13\%}$) C	86.93	13.07
	Re-C4	0.8741	1.60146	0.9927 ($s^{0.01\%}p^{0.11\%}d^{99.88\%}$) Re + 0.1204 ($s^{0.05\%}p^{59.11\%}d^{40.44\%}$) P	98.55	1.45
5	Re-CO(1)	1.3605	1.95505	0.6210 ($s^{22.75\%}p^{17.47\%}d^{59.78\%}$) Re + 0.7838 ($s^{66.29\%}p^{33.70\%}d^{0.01\%}$) C	38.57	61.43
	Re-CO(2)	1.3580	1.95501	0.6212 ($s^{22.67\%}p^{17.24\%}d^{60.08\%}$) Re + 0.7837 ($s^{66.34\%}p^{33.66\%}d^{0.01\%}$) C	38.58	61.42
	Re-P	0.7462	1.85342	0.5576 ($s^{12.29\%}p^{56.45\%}d^{31.26\%}$) Re + 0.8301 ($s^{34.12\%}p^{65.82\%}d^{0.06\%}$) P	31.10	68.90
	Re-N1	0.4982	1.73714	0.9344 ($s^{0.01\%}p^{0.22\%}d^{99.76\%}$) Re + 0.3562 ($s^{0.06\%}p^{99.89\%}d^{0.05\%}$) C	87.31	12.69
	Re-C4	0.8667	1.87750	0.5479 ($s^{12.99\%}p^{42.77\%}d^{44.24\%}$) Re + 0.8365 ($s^{43.82\%}p^{51.17\%}d^{0.00\%}$) C	30.02	69.98
6	Re-CO(1)	1.3528	1.95745	0.6211 ($s^{22.73\%}p^{17.33\%}d^{59.94\%}$) Re + 0.7837 ($s^{66.26\%}p^{33.73\%}d^{0.01\%}$) C	38.58	61.42
	Re-CO(2)	1.3632	1.95628	0.6230 ($s^{22.39\%}p^{17.08\%}d^{60.53\%}$) Re + 0.7822 ($s^{66.31\%}p^{33.68\%}d^{0.01\%}$) C	38.82	61.18
	Re-P	0.8209	1.87785	0.5849 ($s^{13.22\%}p^{56.09\%}d^{30.70\%}$) Re + 0.8111 ($s^{60.13\%}p^{39.70\%}d^{0.16\%}$) P	34.22	65.78
	Re-N1	0.4968	1.73753	0.9358 ($s^{0.05\%}p^{0.39\%}d^{99.69\%}$) Re +	87.58	12.42

				0.3528 ($s^{0.00\%}p^{99.90\%}d^{0.10\%}$) C		
	Re-C4	0.8508	1.88484	0.5471 ($s^{12.74\%}p^{42.90\%}d^{44.36\%}$) Re + 0.8370 ($s^{48.85\%}p^{51.15\%}d^{0.00\%}$) C	29.94	70.06
7	Re-CO(1)	1.2545	1.95271	0.6070 ($s^{25.77\%}p^{19.46\%}d^{54.77\%}$) Re + 0.7947 ($s^{65.94\%}p^{34.06\%}d^{0.00\%}$) C	36.85	63.15
	Re-CO(2)	1.2546	1.95264	0.6070 ($s^{25.78\%}p^{19.48\%}d^{54.74\%}$) Re + 0.7947 ($s^{65.94\%}p^{34.06\%}d^{0.00\%}$) C	36.84	63.16
	Re-CO(3)	1.1177	1.92032	0.5660 ($s^{14.38\%}p^{48.32\%}d^{37.30\%}$) Re + 0.8244 ($s^{66.58\%}p^{33.42\%}d^{0.00\%}$) C	32.03	67.97
	Re-N1	0.4956	1.62272	0.9250 ($s^{0.04\%}p^{2.33\%}d^{97.63\%}$) Re + 0.3799 ($s^{0.02\%}p^{99.98\%}d^{0.01\%}$) N	85.57	14.43
	Re-C4	0.8976	1.90985	0.5496 ($s^{13.13\%}p^{50.14\%}d^{36.73\%}$) Re + 0.8354 ($s^{62.47\%}p^{37.53\%}d^{0.00\%}$) C	30.21	69.79

LANL2DZ for Re atom, 6-31g(d) for all other atoms

Table S22. Second order perturbation interactions that contribute mainly to the ground state stabilization for complexes **1-7** from NBO analysis performed at the PBE1PBE/LANL2DZ[#] level.

Complex	Donor (i)	Acceptor(j)	E(2)(kcalmol^{-1})	E(j)-E(i) a.u	F(i, j) a.u
1	n Re1	σ * Re1-C4	125.13	0.04	0.158
	n N1	n*Re1	72.21	0.68	0.203
	n Re1	π* O1-C1	46.18	0.21	0.099
	n Re1	π* O2-C2	46.17	0.21	0.099
	σ Re1-N1	π* O2-C2	28.22	0.30	0.085
2	n O3	π* Re1-C3	178.54	0.29	0.204
	n O3	π* Re1-C3	177.07	0.31	0.209
	n N1	n*Re1	83.68	0.66	0.216
	n N2	n*Re1	58.21	0.54	0.163
	n O41	π* N3-C4	53.26	0.33	0.121
3	σ N2-C28	π*Re1-N2	101.46	1.63	0.413
	n N2	n*Re1	77.77	0.61	0.202
	π Re1-N2	π* O2-C2	36.92	0.28	0.097
	n Re1	π* O3-C3	33.40	0.25	0.086
	σ Re1-N2	π* O1-C1	26.79	0.25	0.077
4	σ P1-C65	π*Re1-P1	148.79	1.03	0.354
	n N1	n*Re1	75.96	0.63	0.202
	n O41	π*N3-C4	52.63	0.32	0.119
	n Re1	π*O1-C1	51.51	0.19	0.097
	n Re1	π*O2-C2	45.92	0.23	0.101
5	n N1	n*Re1	72.57	0.54	0.182
	n O41	π*Re1-C4	54.78	0.30	0.124
	π N3-C14	π* Re1-C4	50.80	0.30	0.122
	n Re1	π* O1-C1	49.35	0.21	0.102
	n Re1	π* O2-C2	49.31	0.22	0.102
6	n O60	n*P1	175.09	0.65	0.305
	n N2	n*Re1	81.19	0.64	0.209
	n N1	n*Re1	61.38	0.64	0.182
	n Re1	π*O1-C1	52.51	0.20	0.102
	n Re1	π*O2-C2	42.91	0.24	0.101
7	n N2	n*Re1	74.30	0.66	0.204
	n N1	n*Re1	73.71	0.66	0.203
	n Re1	π*O3-C3	33.48	0.24	0.086
	n Re1	π*O1-C1	26.65	0.32	0.087
	n Re1	π*N4-C4	17.80	0.28	0.068

LANL2DZ for Re atom, 6-31g(d) for all other atoms

Scheme of the atom labelling

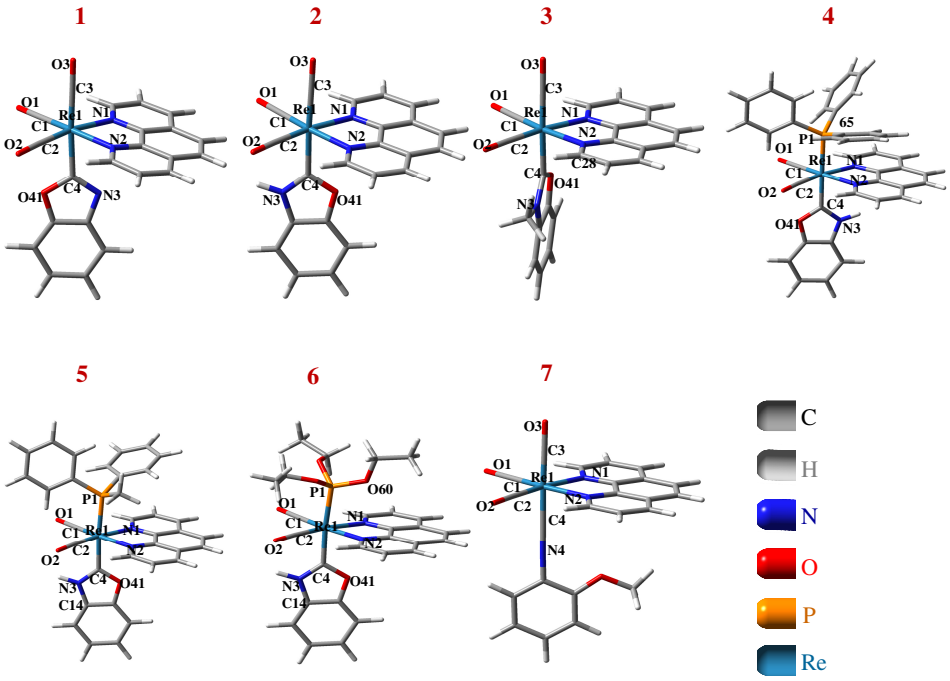


Table S23. Topological properties at the BCPs in Re-CO, Re-N and Re-C4 bonds computed at PBE1PBE/LANL2DZ[#] level. ρ(r) in units of eÅ^{-3}, L(r) in units of eÅ^{-3}, G(r), V(r), H(r) in units of a.u. Å^{-3}.

Re-CO(1) BCP							
Complex	ρ(r)	L(r)	G(r)	H(r)	ε	V(r)	-V(r)/G(r)
1	0.147	-0.132	0.195	-0.0625	0.122	0.257	-1.317
2	0.145	-0.134	0.194	-0.0601	0.063	0.254	-1.309
3	0.144	-0.132	0.191	-0.0594	0.045	0.251	-1.314
4	0.148	-0.138	0.201	-0.0633	0.027	0.265	-1.318
5	0.149	-0.139	0.203	-0.0642	0.070	0.268	-1.320
6	0.148	-0.139	0.202	-0.0628	0.043	0.265	-1.311
7	0.142	-0.132	0.190	-0.0584	0.074	0.249	-1.310
Re-CO(2) BCP							
1	0.147	-0.132	0.195	-0.0625	0.122	0.258	-1.323
2	0.145	-0.134	0.194	-0.0601	0.064	0.254	-1.309
3	0.145	-0.136	0.197	-0.0608	0.039	0.258	-1.309
4	0.149	-0.136	0.200	-0.0645	0.083	0.265	-1.325
5	0.149	-0.137	0.202	-0.0646	0.069	0.267	-1.321
6	0.149	-0.138	0.202	-0.0646	0.100	0.267	-1.321
7	0.142	-0.132	0.190	-0.0584	0.074	0.249	-1.310
Re-L* BCP							
1	0.132	-0.127	0.178	-0.0506	0.026	0.227	-1.275
2	0.128	-0.124	0.170	-0.0469	0.043	0.217	-1.276
3	0.130	-0.125	0.174	-0.0487	0.075	0.223	-1.281
4	0.074	-0.040	0.063	-0.0223	0.111	0.085	-1.349
5	0.077	-0.039	0.064	-0.0240	0.055	0.088	-1.375
6	0.087	-0.049	0.078	-0.0281	0.106	0.106	-1.358
7	0.127	-0.125	0.171	-0.0463	0.013	0.218	-1.274
Re-N(1) BCP							
1	0.079	-0.092	0.101	-0.0095	0.204	0.111	-1.099
2	0.078	-0.089	0.099	-0.0096	0.241	0.109	-1.101
3	0.078	-0.090	0.099	-0.0095	0.225	0.108	-1.090
4	0.078	-0.093	0.102	-0.0093	0.397	0.112	-1.098
5	0.079	-0.092	0.102	-0.0096	0.326	0.111	-1.088
6	0.078	-0.091	0.100	-0.0094	0.316	0.109	-1.090
7	0.077	-0.089	0.098	-0.0095	0.230	0.107	-1.091
Re-C(4) BCP							
1	0.106	-0.064	0.100	-0.0361	0.105	0.136	-1.360
2	0.105	-0.083	0.116	-0.0333	0.131	0.149	-1.284
3	0.100	-0.078	0.108	-0.0301	0.133	0.138	-1.277
4	0.119	-0.089	0.132	-0.0434	0.111	0.175	-1.325
5	0.118	-0.087	0.130	-0.0430	0.126	0.173	-1.330
6	0.116	-0.087	0.128	-0.0414	0.140	0.169	-1.320
7	0.109	-0.098	0.133	-0.0349	0.011	0.168	-1.263

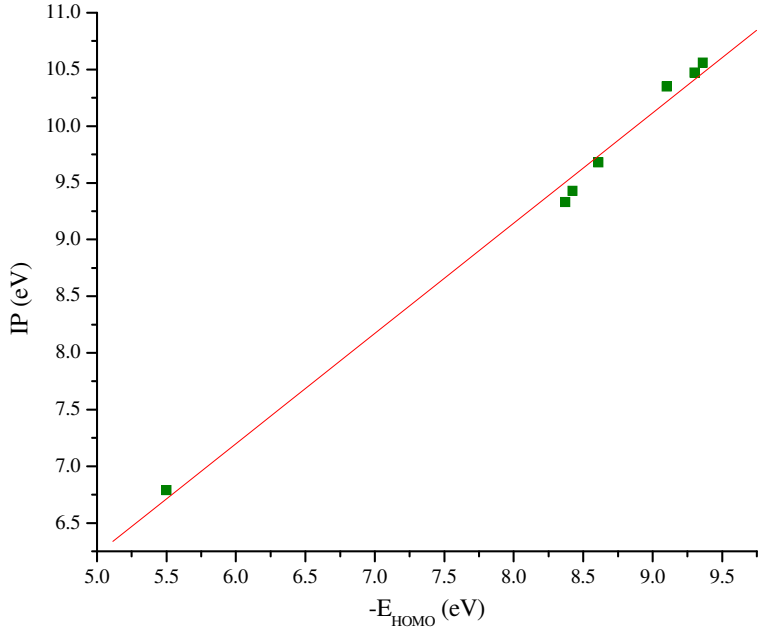
* L= CO(3) for 1-3 and 7
L=P for 4-6

LANL2DZ for Re atom, 6-31g(d) for all other atoms

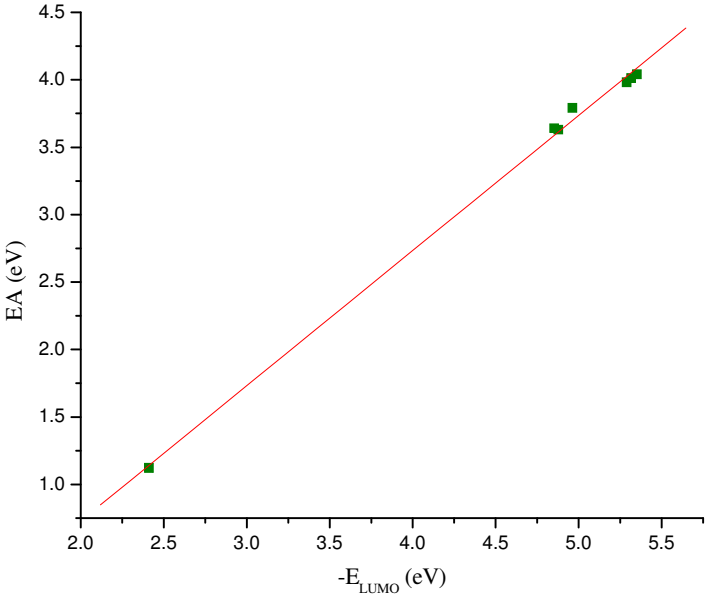
Table S24. Selected bond parameters for complexes **1-7** in the low lying triplet excited state at the TDDFT and CIS methods.

Bond Parameters	1		2		3		4		5		6		7	
	TDDFT	**CIS**	**TDDFT**	**CIS**	**TDDFT**	**CIS**	**TDDFT**	**CIS**	**TDDFT**	**CIS**	**TDDFT**	**CIS**	**TDDFT**	**CIS**
Re-C1(Å)	1.929	1.967	1.926	1.973	1.935	1.979	1.908	1.913	1.964	1.904	1.905	1.909	1.933	1.975
Re-C2(Å)	1.929	1.925	1.926	1.921	1.922	1.926	1.968	1.978	1.898	1.977	1.960	1.976	1.933	1.934
Re-C3(Å)	2.018	2.027	1.979	2.007	1.975	2.004	-	-	-	-	-	-	1.979	2.010
Re-C4(Å)	2.053	2.080	2.122	2.124	2.144	2.138	2.081	2.083	2.080	2.090	2.089	2.093	2.062	2.049
Re-N1(Å)	2.177	2.169	2.175	2.185	2.182	2.189	2.069	2.070	2.189	2.070	2.072	2.060	2.180	2.188
Re-N2(Å)	2.177	2.097	2.175	2.069	2.162	2.062	2.195	2.180	2.071	2.171	2.186	2.172	2.180	2.075
Re-P1(Å)	-	-	-	-	-	-	2.542	2.548	2.513	2.518	2.448	2.461	-	-
C1-Re-C2(°)	87.52	89.92	90.77	90.82	90.97	91.85	91.50	91.48	90.40	89.35	89.79	89.12	90.77	91.17
N1-Re-N2(°)	76.61	77.40	74.96	77.18	74.72	77.13	77.35	77.63	77.35	77.79	77.15	77.65	74.87	77.14

Figure S1. (a) The correlation between the calculated HOMO energies and the IP values. (b) The correlation between the calculated LUMO energies and the EA values computed at the PBE1PBE/LANL2DZ# level.



(a)



(b)

LANL2DZ for Re atom, 6-31g(d) for all other atoms

Figure S2. Ground state stabilizing interactions of complexes **1-7**, showing n → σ* and n → n* interactions.

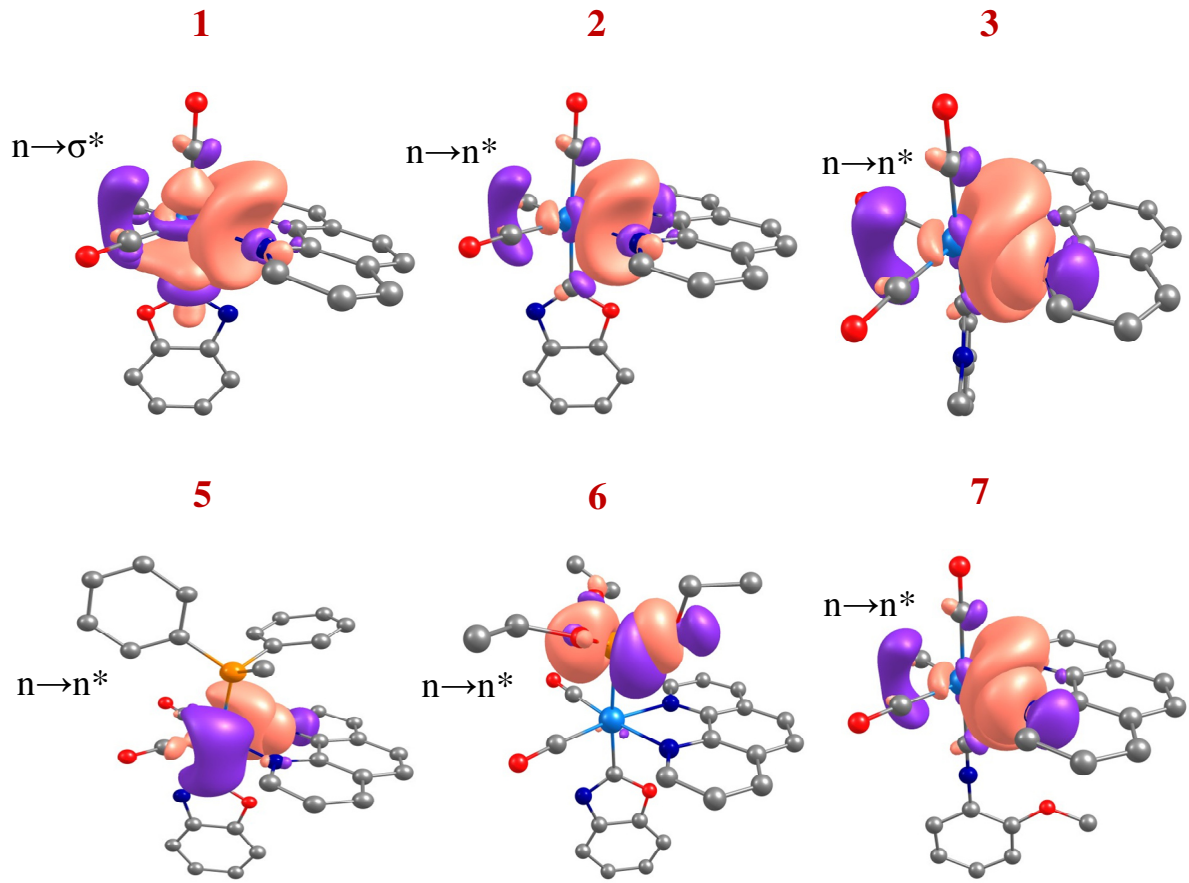


Figure S3. a) Molecular graph of the complexes **1-7**. All critical points are shown, as are attractors by greater circles: BCPs, small red circles; RCPs, yellow ones. The bond paths are also shown. b) Contour line diagrams of the Laplacian distribution in the plane contains the Re, CO(3) and benzoxazole ligands.

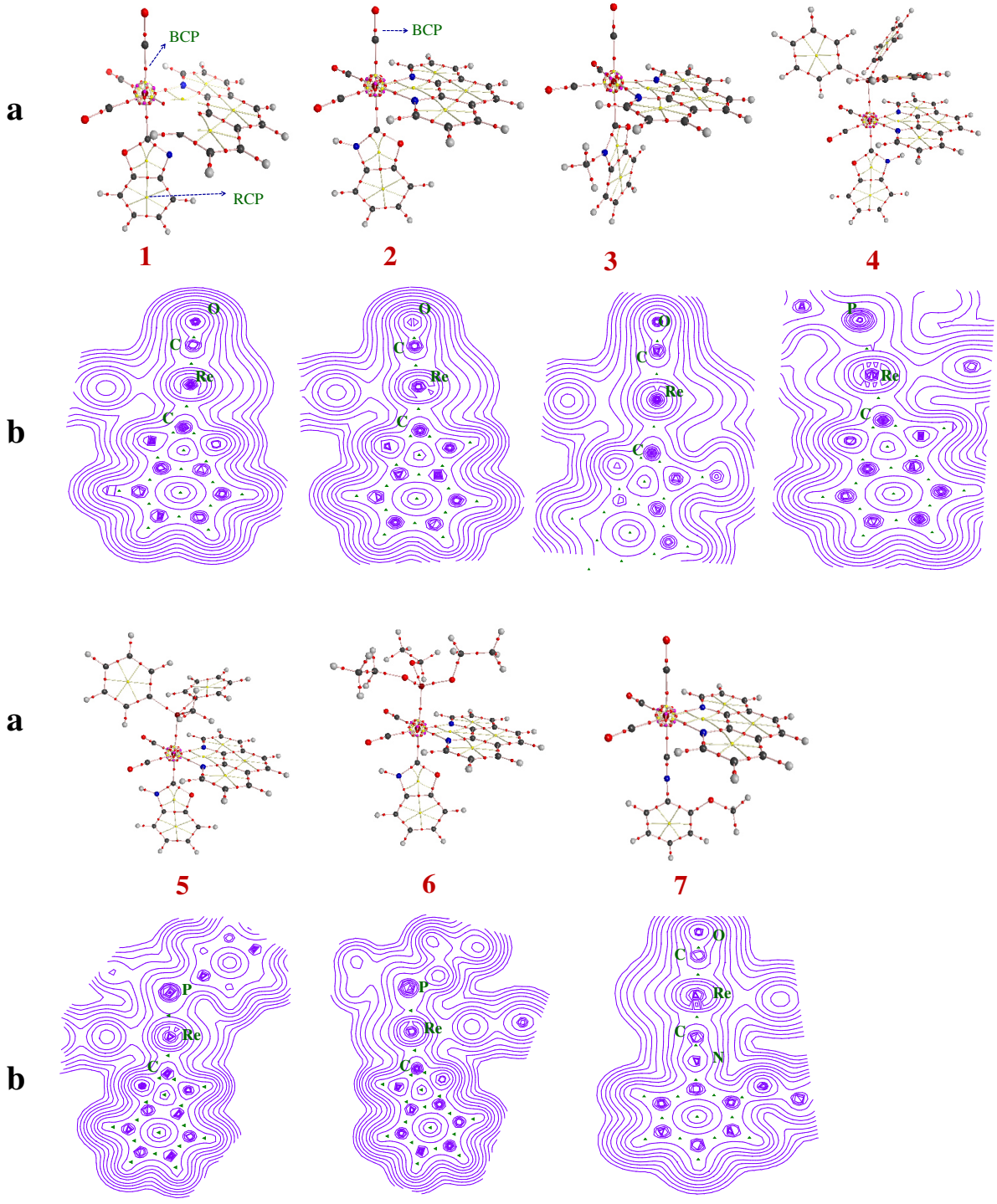


Figure S4. Effect of Solvent on Absorption Spectra of Complexes **1-7** computed at PBE1PBE/LANL2DZ level.

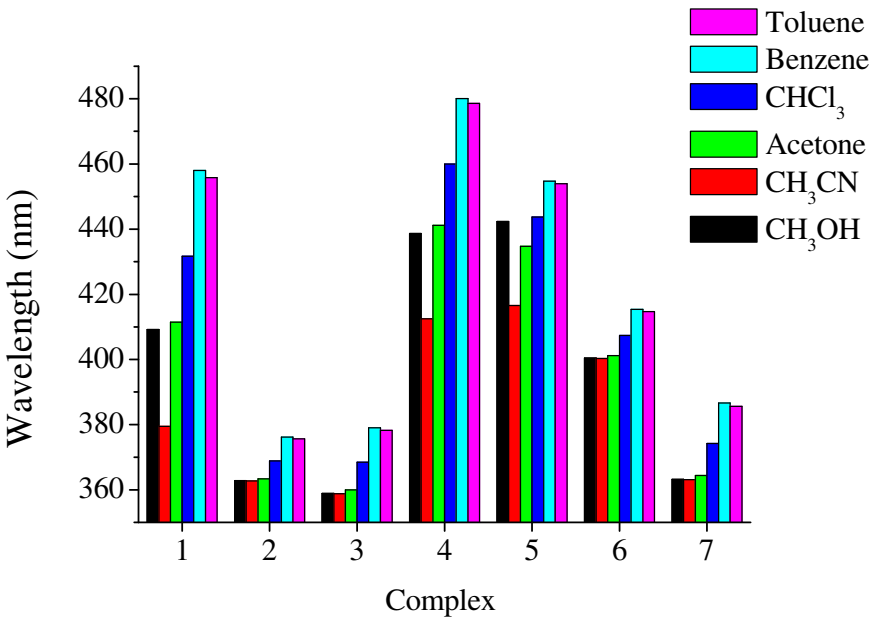


Figure S5. Effect of Solvent on Phosphorescence Spectra of Complexes **1-7** computed at PBE1PBE/LANL2DZ level.

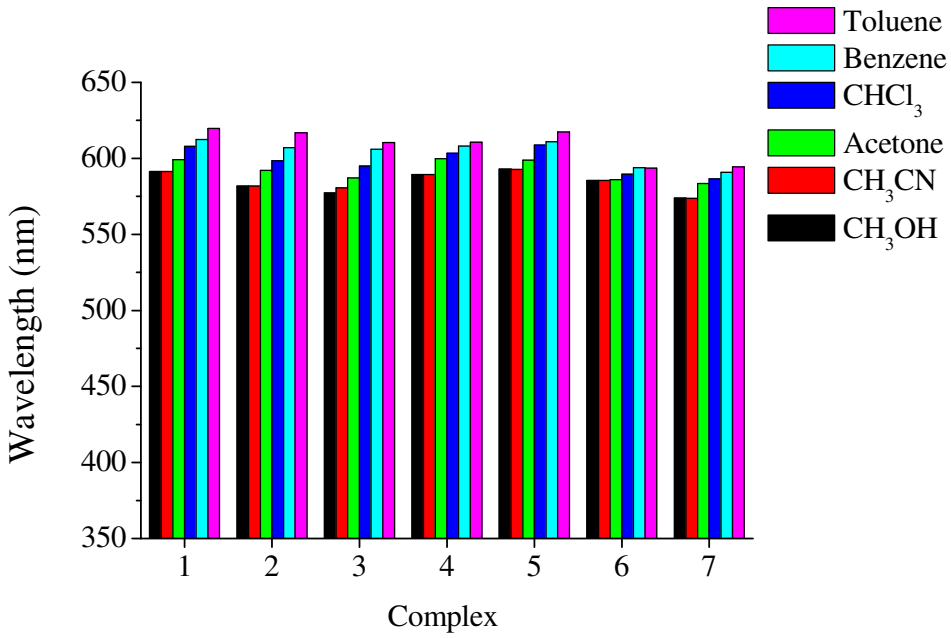


Figure S6. Natural Transition Orbitals (NTOs) for the Complex **3** and **4** illustrating the nature of optically active singlet excited states in the absorption bands. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 50% to each excited state. All transitions have mixed ^{1}MLCT/^{1}LLCT character.

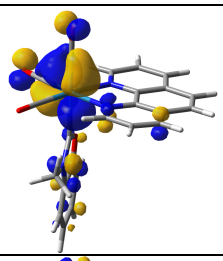
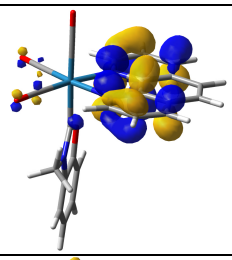
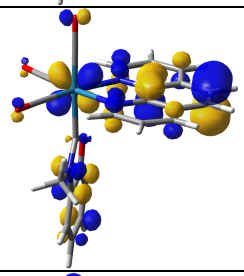
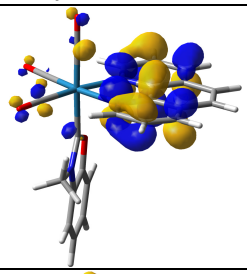
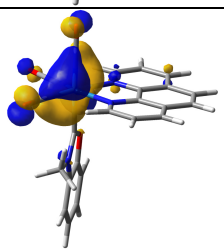
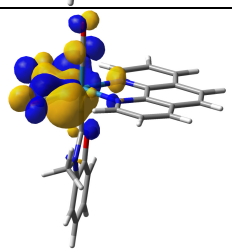
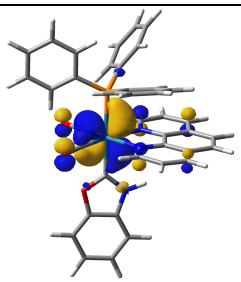
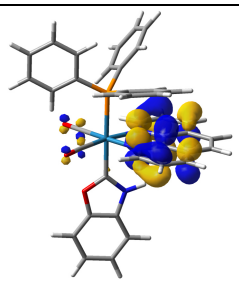
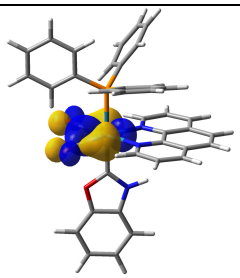
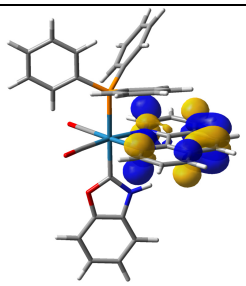
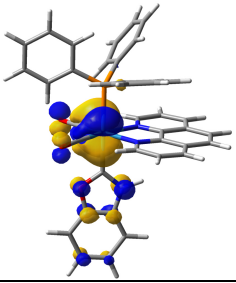
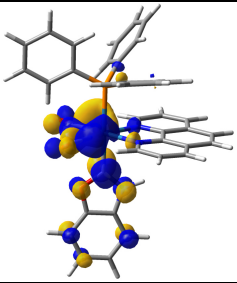
Complex	λ_{cal} (nm)		Hole	Electron
3	358.8	S_1 W=0.98		
	296.1	S_8 W=0.54		
	271.3	S_{13} W=0.62		
4	412.5	S_2 W=0.88		
	338.9	S_6 W=0.99		
	319.7	S_8 W=0.97		

Figure S7. Natural Transition Orbitals (NTOs) for the Complex **5** and **6** illustrating the nature of optically active singlet excited states in the absorption bands. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 50% to each excited state. All transitions have mixed ^{1}MLCT/^{1}LLCT character.

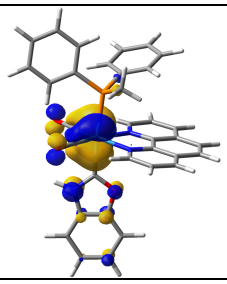
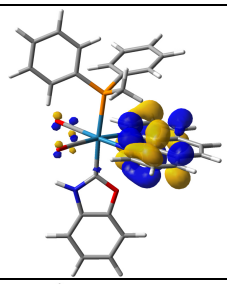
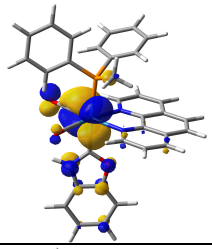
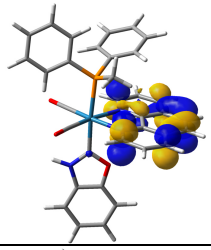
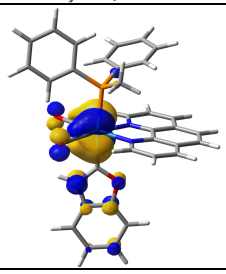
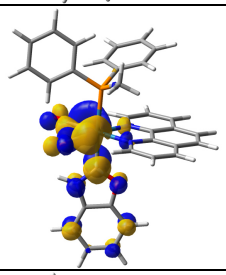
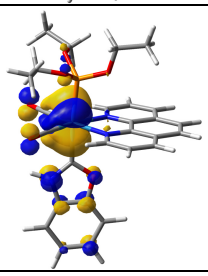
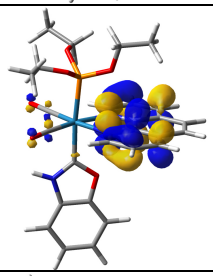
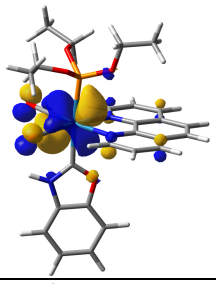
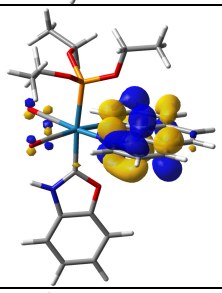
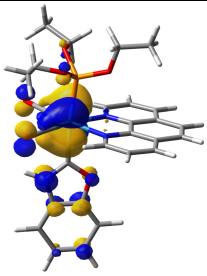
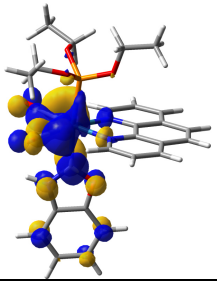
Complex	λ_{cal} (nm)		Hole	Electron
5	416.6	S_1 W=0.99		
	380.4	S_3 W=0.61		
	323.6	S_8 W=0.96		
6	400.3	S_1 W=0.99		
	357.8	S_3 W=0.55		
	312.6	S_8 W=0.96		

Figure S8. Natural Transition Orbitals (NTOs) for the Complex **7** illustrating the nature of optically active singlet excited states in the absorption bands. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 50% to each excited state. All transitions have mixed ^{1}MLCT/^{1}LLCT character.

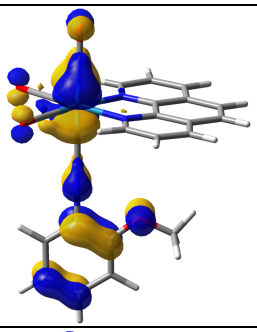
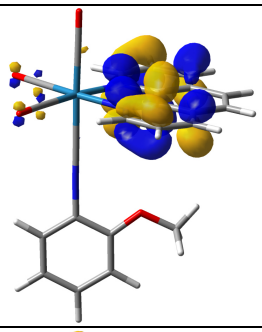
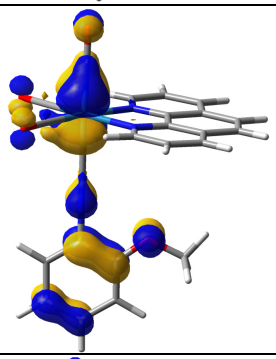
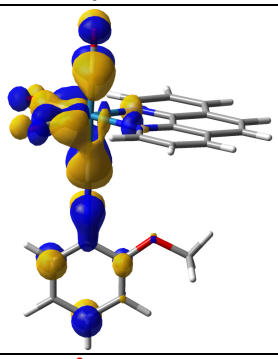
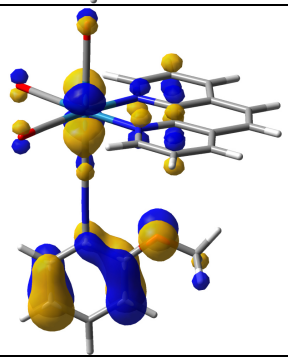
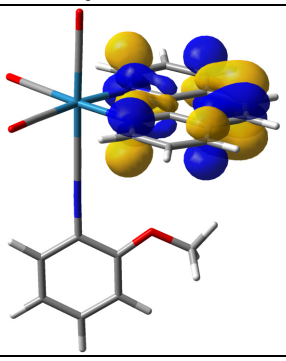
Complex	λ_{cal} (nm)		Hole	Electron
7	363.1	S_1 W=0.99		
	311.6	S_5 W=0.85		
	292.9	S_{10} W=0.56		

Figure S9. The schematic energy diagrams of the molecular orbital related to the phosphorescence of **1**-**7**. Assignments of bands are given in Table 5.