Electronic Supplementary Information

Luminescent Rhenium(I) Tricarbonyl Complexes with Pyrazolylamidino Ligands: Photophysical, Electrochemical, and Computational Studies

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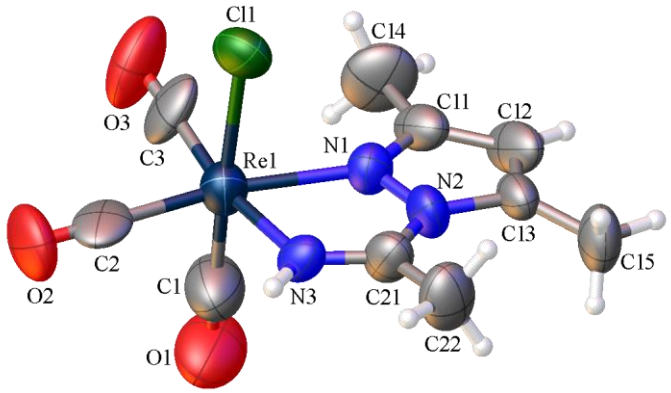
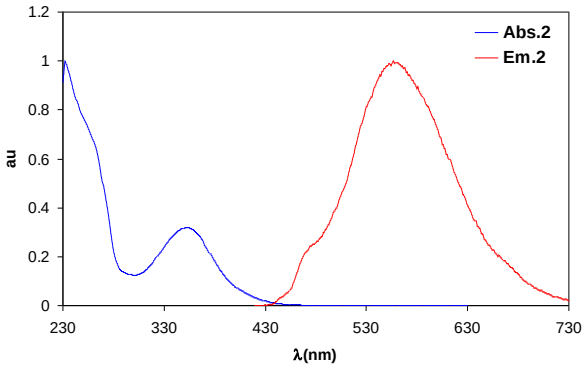


Figure S1. Perspective view of *fac*-[ReCl(CO)$_3$(NH=C(Me)dmpz-κ^2*N*,*N*)], **2,** showing the atom numbering. Thermal ellipsoids are drawn at 50% probability.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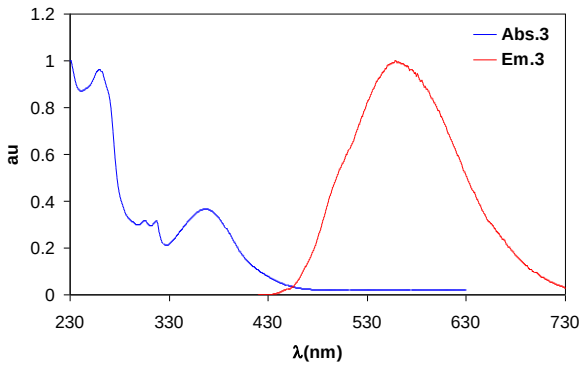
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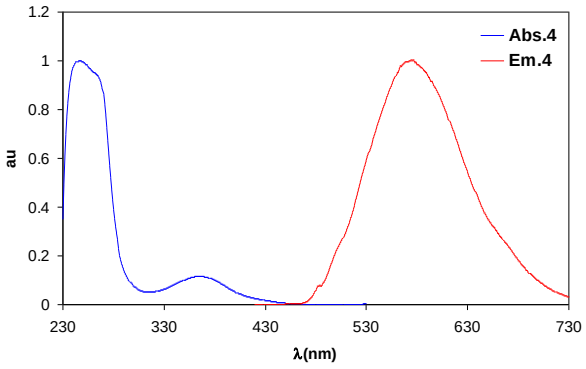
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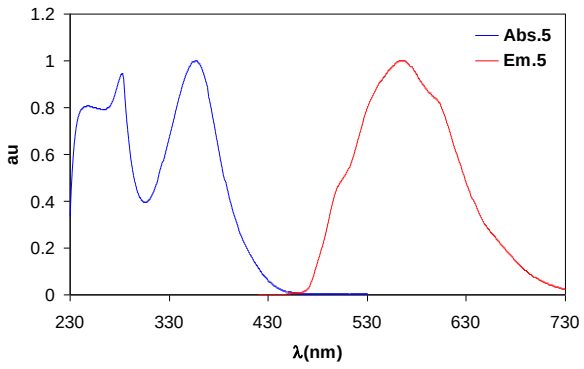
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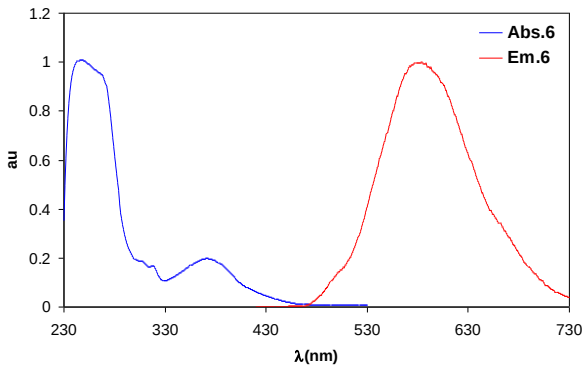
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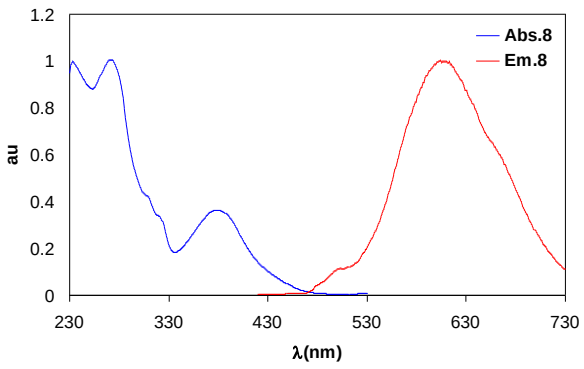
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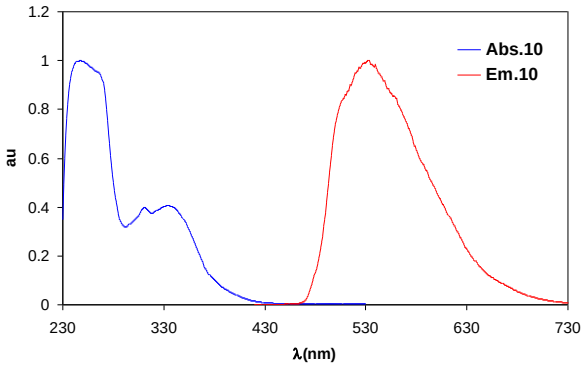
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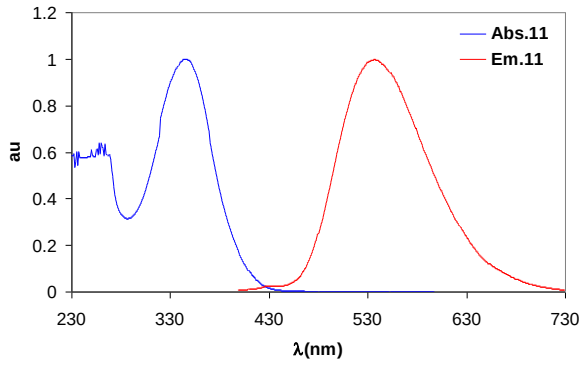
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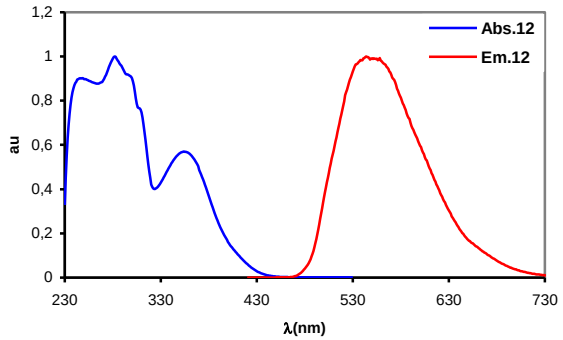


Figure S2. Normalized emission (red) and absorption (blue) spectra recorded in CH_2Cl_2 of complexes **2-6**, **8**, **10-12** at 298 K. As indicated in Table 1, not reliable spectra could be obtained for **7** due to its instability in CH_2Cl_2 solution.

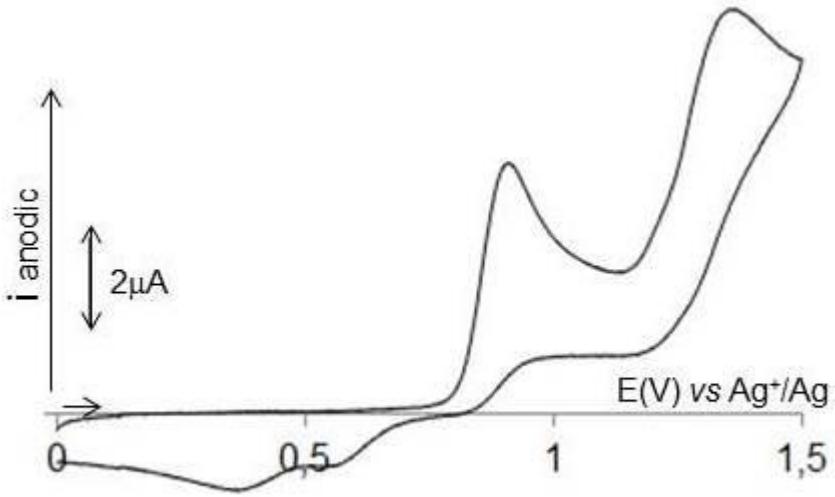


Figure S3. Cyclic voltammogram recorded in CH_2Cl_2 solution of 10 mM **5**. Scan rate: 100 mV/s.

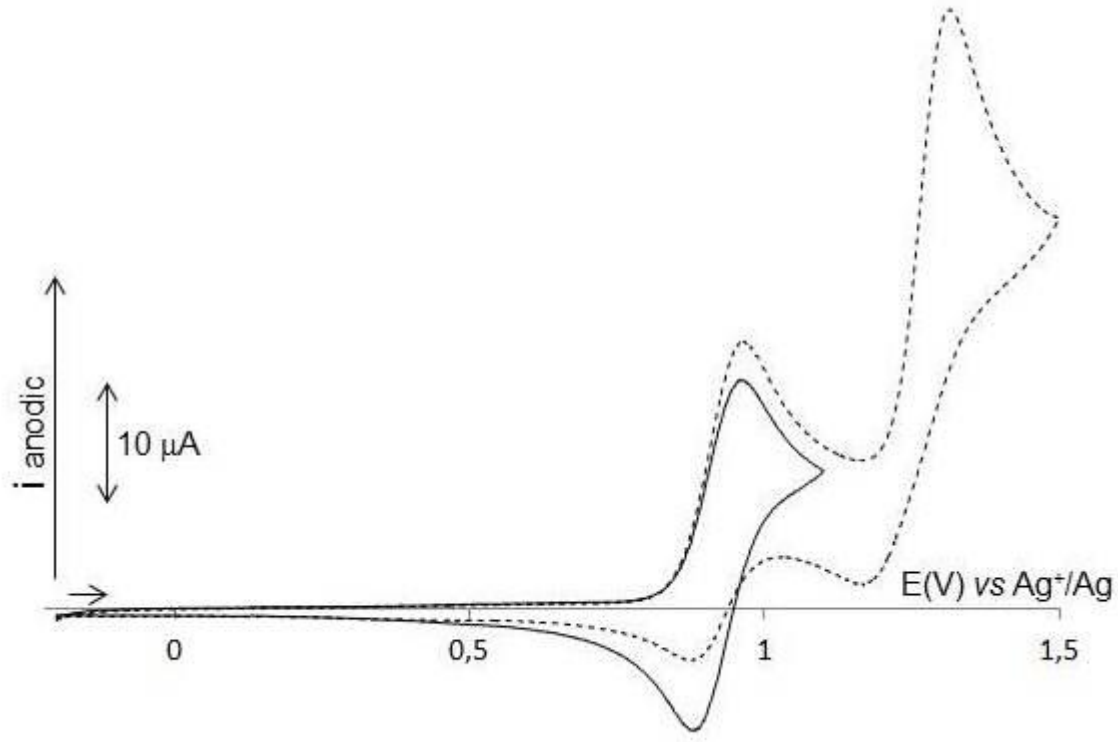


Figure S4. Cyclic voltammogram recorded in MeCN solution of 8.6 mM *fac*-$[ReBr(CO)_3(dmpzH)_2]$. Scan rate: 100 mV/s.

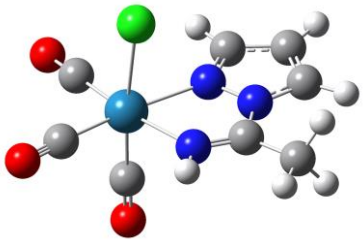
Table S1. Deviation from the geometry found by X-ray diffraction for selected bond distances of complex **1** calculated with different functionals and using LANL2DZ for the Re atom and 6-31G+(d,p) for the rest of the atoms (Calculated distance - experimental distance).

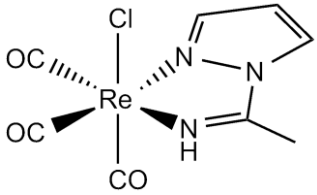
Functional	Re1-Cl1	Re1-N3	Re1-N1	Re1-C1	Re1-C2	Re1-C3	Average deviation
B3LYP	0.040	0.008	0.010	0.005	0.041	0.002	0.018
BMK	0.036	0.010	0.011	0.011	0.047	0.006	0.020
CAM-B3LYP	0.022	0.003	-0.002	-0.003	0.038	-0.004	0.012
M06	0.019	0.009	-0.002	-0.0002	0.038	-0.005	0.012
PBE	0.019	-0.013	-0.008	0.003	0.034	-0.005	0.014
TPSS	0.018	-0.016	-0.014	0.010	0.043	0.004	0.018
WB97XD	0.026	0.012	0.002	-0.010	0.032	-0.011	0.016
PBE1PBE	-0,003	-0.018	-0.021	-0.008	0.030	-0.011	0.015

Table S2. Deviation from the geometry found by X-ray diffraction for selected bond distances of complex **1** calculated with different basis sets and using the PBE1PBE functional (Calculated distance - experimental distance).

Basis set	Re1-Cl1	Re1-N3	Re1-N1	Re1-C1	Re1-C2	Re1-C3	Average deviation
LANL2DZ (Re) 6-31G+(d,p) (rest)	-0.003	-0.018	-0.021	-0.008	0.030	-0.011	0.015
LANL2DZ (Re) 6-311G+(d,p) (rest)	0.010	-0.021	-0.024	-0.009	0.031	-0.010	0.018
SDD (Re) 6-31G+(d,p) (rest)	0.003	-0.001	-0.003	0.004	0.041	0.001	0.009
SDD (Re) 6-311G+(d,p) (rest)	0.009	-0.002	-0.002	0.004	0.041	0.001	0.010
TZVPDD	-0.043	0.013	0.028	0.001	0.034	-0.006	0.021

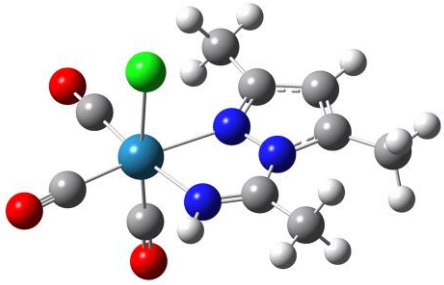
Table S3. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **1** at the PBE1PBE Level

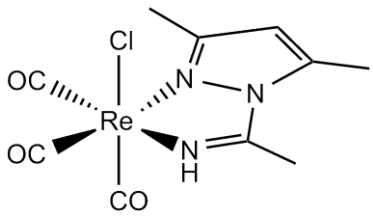




		Contribution (%)				
Orbital	Energy (eV):	Re:	Cl:	CO:	amidino:	main bond type
HOMO-4	-7.76	12.29	55.89	3.97	27.85	d(Re) + p(Cl) + π(amidino)
HOMO-3	-7.66	9.84	58.90	3.35	27.91	d(Re) + p(Cl) + π(amidino)
HOMO-2	-6.98	68.90	0.53	28.57	2.00	d(Re) + π(CO)
HOMO-1	-6.40	46.90	25.98	20.78	6.33	d(Re) + p(Cl) + π(CO)
HOMO	-6.32	47.08	25.77	22.84	4.32	d(Re) + p(Cl) + π(CO)
LUMO	-2.04	4.60	1.68	5.82	87.91	π*(amidino)
LUMO+1	-0.55	29.29	1.08	65.50	4.14	p(Re) + π*(CO)
LUMO+2	-0.31	27.97	2.90	61.25	7.89	p(Re) + π*(CO)

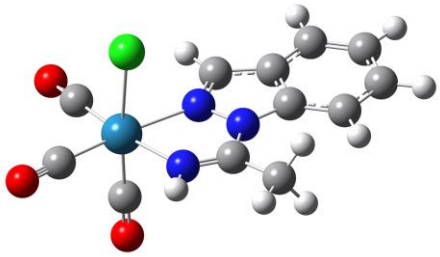
Table S4. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **2** at the PBE1PBE Level

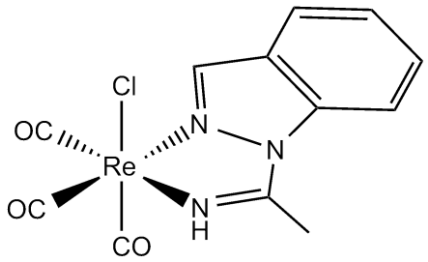




		Contribution (%)				
Orbital	Energy (eV):	Re:	Cl:	CO:	amidino:	main bond type
HOMO-4	-7.60	6.55	45.17	2.21	46.07	p(Cl) + π(amidino)
HOMO-3	-7.43	5.30	54.17	1.88	38.65	p(Cl) + π(amidino)
HOMO-2	-6.90	67.66	0.26	28.86	3.22	d(Re) + π(CO)
HOMO-1	-6.32	46.95	22.99	20.99	9.07	d(Re) + p(Cl) + π(CO)
HOMO	-6.26	47.34	24.58	22.89	5.20	d(Re) + p(Cl) + π(CO)
LUMO	-1.87	5.72	1.80	6.78	85.70	π*(amidino)
LUMO+1	-0.45	27.90	1.02	66.44	4.63	p(Re) + π*(CO)
LUMO+2	-0.25	26.72	2.72	60.20	10.36	p(Re) + π*(CO)

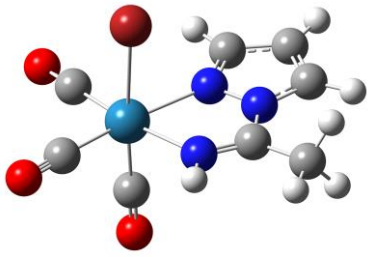
Table S5. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **3** at the PBE1PBE Level

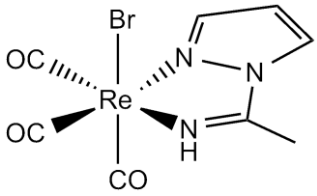




		Contribution (%)				
Orbital	Energy (eV):	Re:	Cl:	CO:	amidino:	main bond type
HOMO-4	-7.55	4.21	39.33	1.50	54.95	p(Cl) + π(amidino)
HOMO-3	-7.20	3.00	18.84	1.26	76.89	p(Cl) + π(amidino)
HOMO-2	-6.95	66.34	0.24	27.71	5.71	d(Re) + π(CO)
HOMO-1	-6.36	45.98	23.72	20.47	9.83	d(Re) + p(Cl) + π(CO)
HOMO	-6.29	46.34	24.92	22.16	6.58	d(Re) + p(Cl) + π(CO)
LUMO	-2.12	3.97	1.58	5.25	89.20	π*(amidino)
LUMO+1	-0.96	0.96	0.13	2.94	95.97	π*(amidino)
LUMO+2	-0.53	28.55	1.08	66.23	4.15	p(Re) + π*(CO)

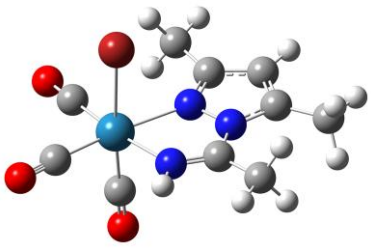
Table S6. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **4** at the PBE1PBE Level

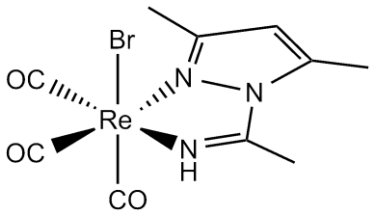




		Contribution (%)				
Orbital	Energy (eV):	Re:	Br:	CO:	amidino:	main bond type
HOMO-4	-7.46	22.14	51.4	7.8	18.66	d(Re) + p(Br) + π(amidino)
HOMO-3	-7.35	17.76	54.04	6.07	22.13	d(Re) + p(Br) + π(amidino)
HOMO-2	-6.99	68.7	0.52	28.53	2.26	d(Re) + π(CO)
HOMO-1	-6.34	38.37	39.86	16.81	4.95	d(Re) + p(Br) + π(CO)
HOMO	-6.28	38.97	38.68	19.04	3.3	d(Re) + p(Br) + π(CO)
LUMO	-2.05	4.4	2.48	5.83	87.29	π*(amidino)
LUMO+1	-0.59	30.24	1.02	64.71	4.03	p(Re) + π*(CO)
LUMO+2	-0.36	27.72	4.52	59.84	7.92	p(Re) + π*(CO)

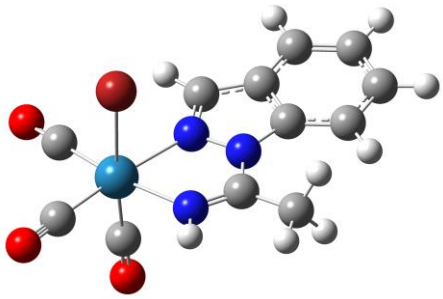
Table S7. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **5** at the PBE1PBE Level

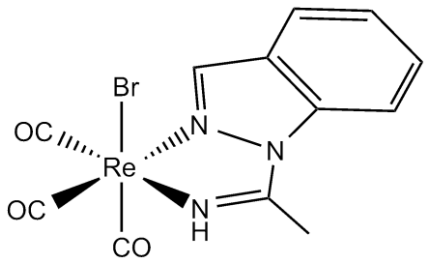




		Contribution (%)				
Orbital	Energy (eV):	Re:	Br:	CO:	amidino:	main bond type
HOMO-4	-7.34	16.88	48.95	6.14	28.02	p(Br) + π(amidino)
HOMO-3	-7.16	14.14	52.8	4.91	28.15	p(Br) + π(amidino)
HOMO-2	-6.91	64.93	1.81	27.89	5.37	d(Re) + π(CO)
HOMO-1	-6.27	39.56	35.73	17.49	7.22	d(Re) + p(Br) + π(CO)
HOMO	-6.22	39.73	36.95	19.31	4.01	d(Re) + p(Br) + π(CO)
LUMO	-1.87	5.45	2.7	6.81	85.03	π*(amidino)
LUMO+1	-0.49	28.91	0.98	65.55	4.56	p(Re) + π*(CO)
LUMO+2	-0.31	26.48	4.2	58.97	10.35	p(Re) + π*(CO)

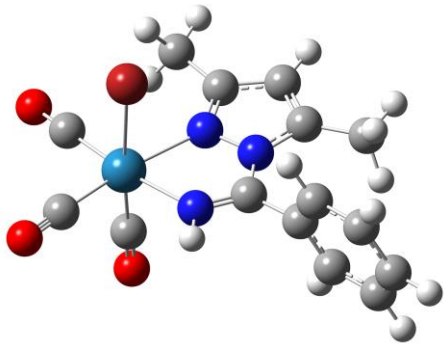
Table S8. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **6** at the PBE1PBE Level

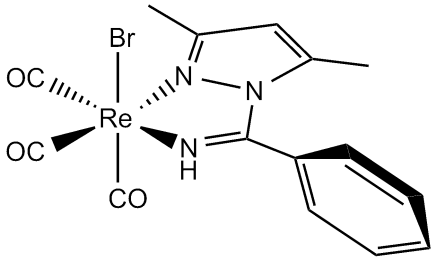




		Contribution (%)				
Orbital	Energy (eV):	Re:	Br:	CO:	amidino:	main bond type
HOMO-3	-7.09	14.84	30.61	5.64	48.91	d(Re) + p(Br) + π(amidino)
HOMO-2	-6.95	57.13	3.88	24.07	14.92	d(Re) + π(CO) + π(amidino)
HOMO-1	-6.32	38.54	36.9	17.02	7.54	d(Re) + p(Br) + π(CO)
HOMO	-6.26	38.75	37.42	18.6	5.22	d(Re) + p(Br) + π(CO)
LUMO	-2.13	3.84	2.31	5.27	88.58	π*(amidino)
LUMO+1	-0.96	0.98	0.21	3.07	95.74	π*(amidino)
LUMO+2	-0.57	29.53	1.02	65.4	4.06	p(Re) + π*(CO)
LUMO+3	-0.36	26.62	4.53	58.19	10.65	p(Re) + π*(CO)

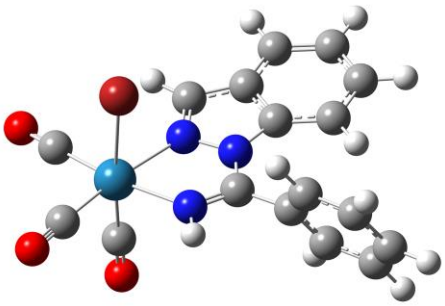
Table S9. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **7** at the PBE1PBE Level

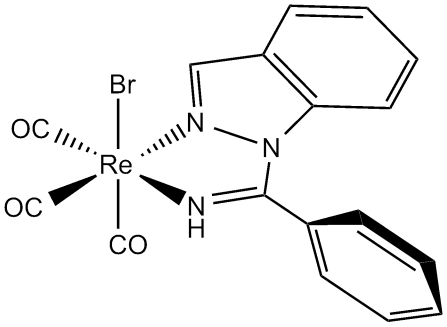




		Contribution (%)				
Orbital	Energy (eV):	Re:	Br:	CO:	amidino:	main bond type
HOMO-6	-7.82	0.9	1.62	0.45	97.03	π(amidino)
HOMO-5	-7.74	2.09	2.18	0.81	94.92	π(amidino)
HOMO-4	-7.33	15.39	45.45	5.81	33.35	d(Re) + p(Br) + π(amidino)
HOMO-3	-7.17	13.69	52.25	4.69	29.37	d(Re) + p(Br) + π(amidino)
HOMO-2	-6.93	65.15	1.67	27.82	5.37	d(Re) + π(CO)
HOMO-1	-6.29	39.26	36.34	17.26	7.14	d(Re) + p(Br) + π(CO)
HOMO	-6.24	39.52	36.86	19.34	4.28	d(Re) + p(Br) + π(CO)
LUMO	-2.01	4.72	2.49	6.06	86.74	π*(amidino)
LUMO+1	-0.84	5.83	0.46	7.79	85.92	π*(amidino)
LUMO+2	-0.53	1.5	0.24	3.06	95.19	π*(amidino)
LUMO+3	-0.47	26.04	1.34	61.75	10.88	p(Re) + π*(CO) + π*(amidino)

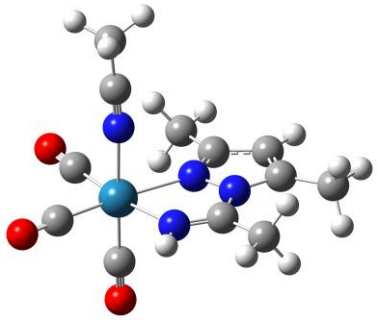
Table S10. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **8** at the PBE1PBE Level

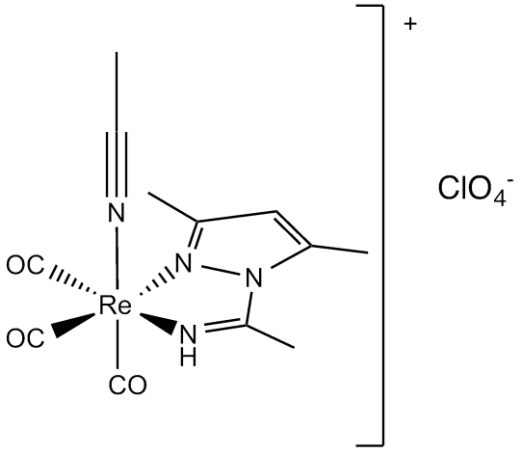




		Contribution (%)				
Orbital	Energy (eV):	Re:	Br:	CO:	amidino:	main bond type
HOMO-5	-7.55	14.5	20.43	5.43	59.65	d(Re) + p(Br) + π(amidino)
HOMO-4	-7.35	12.98	41.12	4.69	41.2	d(Re) + p(Br) + π(amidino)
HOMO-3	-7.07	15.01	30.52	5.73	48.74	d(Re) + p(Br) + π(amidino)
HOMO-2	-6.97	56.7	3.83	23.8	15.68	d(Re) + π(CO) + π(amidino)
HOMO-1	-6.32	38.19	36.44	16.86	8.52	d(Re) + p(Br) + π(CO)
HOMO	-6.28	38.57	38.32	18.65	4.46	d(Re) + p(Br) + π(CO)
LUMO	-2.19	3.8	2.32	5.2	88.69	π*(amidino)
LUMO+1	-1.24	0.48	0.04	1.85	97.63	π*(amidino)
LUMO+2	-0.71	13.12	0.61	23.48	62.79	p(Re) + π*(CO) + π*(amidino)

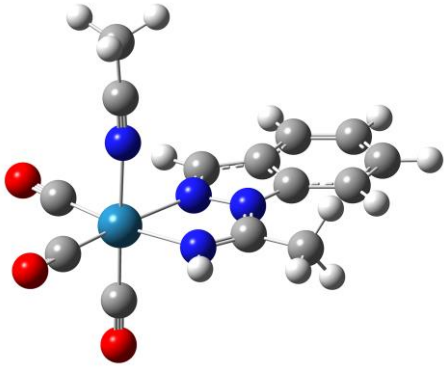
Table S11. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **9** at the PBE1PBE Level

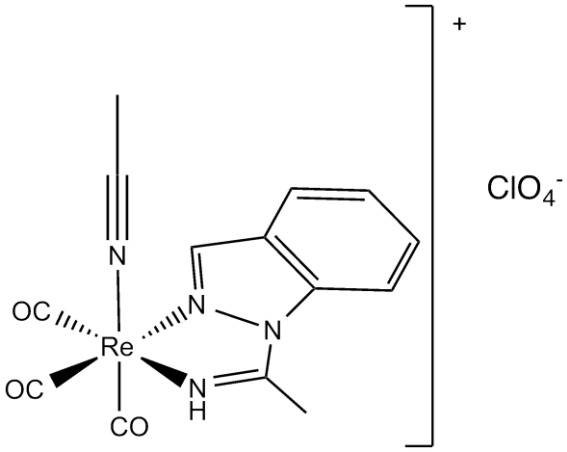




		Contribution (%)				
Orbital	Energy (eV):	Re:	MeCN:	CO:	amidino:	main bond type
HOMO-3	-8.39	6.21	1.44	2.11	90.25	π(amidino)
HOMO-2	-7.5	69.58	0	27.9	2.52	d(Re) + π(CO)
HOMO-1	-7.17	59.02	4.74	23.04	13.21	d(Re) + π(CO) + π(amidino)
HOMO	-7.11	54	4.09	21.28	20.63	d(Re) + π(CO) + π(amidino)
LUMO	-2.37	5.65	0.5	7.38	86.48	π*(amidino)
LUMO+1	-1.27	26.08	18.09	51.59	4.23	p(Re) + π*(CO) + π*(MeCN)
LUMO+2	-0.93	19.19	25.13	51.32	4.36	p(Re) + π*(CO) + π*(MeCN)

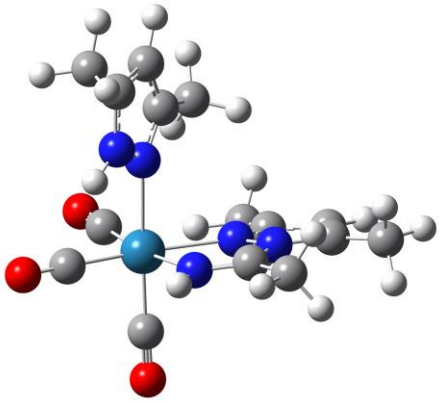
Table S12. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **10** at the PBE1PBE Level

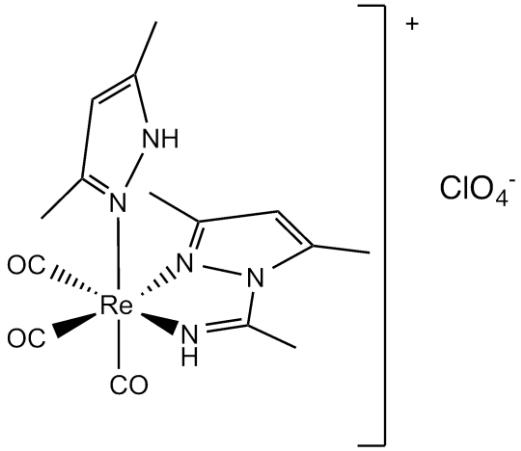




		Contribution (%)				
Orbital	Energy (eV):	Re:	MeCN:	CO:	amidino:	main bond type
HOMO-4	-8.38	10.66	2.24	3.39	83.71	d(Re) + π(amidino)
HOMO-3	-7.79	15.58	1.72	5.37	77.33	d(Re) + π(amidino)
HOMO-2	-7.54	68.75	0.01	27.13	4.12	d(Re) + π(CO)
HOMO-1	-7.21	57.16	4.63	22.67	15.54	d(Re) + π(CO) + π(amidino)
HOMO	-7.12	45.5	3.47	17.45	33.58	d(Re) + π(CO) + π(amidino)
LUMO	-2.6	4.23	0.45	5.9	89.42	π*(amidino)
LUMO+1	-1.36	10.51	6.9	20.56	62.03	π*(CO) + π*(amidino)
LUMO+2	-1.31	17.45	9.94	35.79	36.82	p(Re) + π*(CO) + π*(amidino)
LUMO+3	-0.97	19.45	23.74	51.89	4.91	p(Re) + π*(CO) + π*(MeCN)

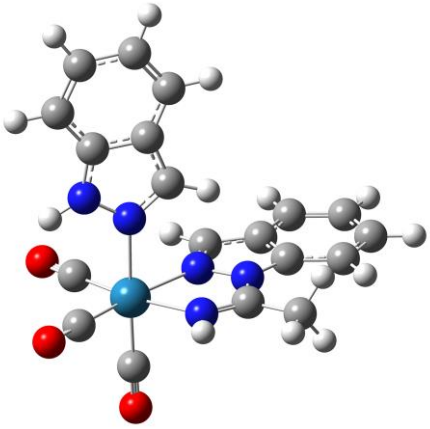
Table S13. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **11** at the PBE1PBE Level

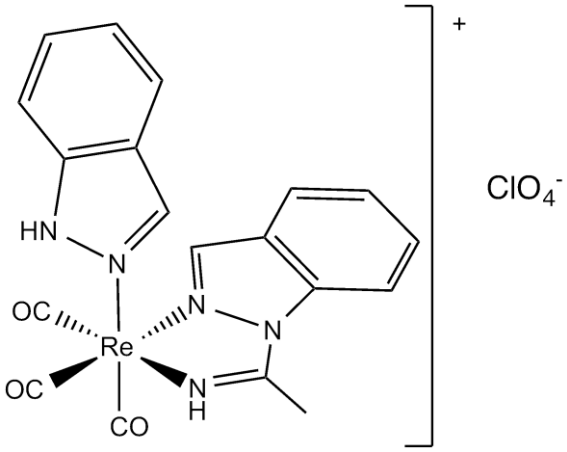




		Contribution (%)				
Orbital	Energy (eV):	Re:	dmpz:	CO:	amidino:	main bond type
HOMO-4	-8.10	6.49	74.87	2.42	16.22	π(dmpz) + π(amidino)
HOMO-3	-7.85	1.79	90.14	0.91	7.15	π(dmpz) + π(amidino)
HOMO-2	-7.52	68.78	0.84	28.62	1.76	d(Re) + π(CO)
HOMO-1	-7.20	59.52	0.98	24.36	15.14	d(Re) + π(CO) + π(amidino)
HOMO	-6.88	46.28	22.68	19.57	11.48	d(Re) + π(dmpz) + π(CO)
LUMO	-2.34	5.56	1.36	7.55	85.53	π*(amidino)
LUMO+1	-1.14	29.03	3.64	62.59	4.74	p(Re) + π*(CO)
LUMO+2	-0.82	18.50	17.13	56.85	7.52	p(Re) + π*(dmpz) + π*(CO)

Table S14. Frontier Molecular Orbital Compositions (%) in the Ground State for Complex **12** at the PBE1PBE Level





		Contribution (%)				
Orbital	Energy (eV):	Re:	indz:	CO:	amidino:	main bond type
HOMO-2	-7.22	46.02	2.75	17.87	33.35	d(Re) + π(CO) + π(amidino)
HOMO-1	-7.13	4.93	91	1.56	2.51	π(indazol)
HOMO	-7	42.34	30.35	18.64	8.67	d(Re) + π(CO) + π(indazol)
LUMO	-2.67	4.47	0.86	6.17	88.49	π*(amidino)
LUMO+1	-1.77	6.81	79.25	12.68	1.25	π*(indazol)
LUMO+2	-1.39	1.1	0.18	3.9	94.83	π*(amidino)

Table S15. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **1**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO → LUMO	0.70	3.21	386	0.0035		MLCT/LLCT/XLCT
S_2	HOMO-1 → LUMO	0.69	3.39	366	0.0964	360	MLCT/LLCT/XLCT
S_8	HOMO-4 → LUMO HOMO-3 → LUMO	0.64 0.27	4.76	261	0.1178	264	MLCT/XLCT/ILCT

Table S16. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **2**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO → LUMO	0.69	3.33	372	0.0033		MLCT/LLCT/XLCT
S_2	HOMO-1 → LUMO	0.69	3.49	356	0.1067	352	MLCT/LLCT/XLCT
S_7	HOMO-3 → LUMO	0.67	4.62	268	0.0855	261	XLCT/ILCT
S_8	HOMO-4 → LUMO	0.67	4.76	261	0.0850		XLCT/ILCT

Table S17. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **3**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO → LUMO	0.68	3.17	391	0.0031		MLCT/LLCT/XLCT
S_2	HOMO-1 → LUMO	0.67	3.34	371	0.1680	367	MLCT/LLCT/XLCT
S_4	HOMO-3 → LUMO	0.66	4.24	292	0.1652	304	XLCT/ILCT

Table S18. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **4**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO → LUMO	0.69	3.18	389	0.0023		MLCT/LLCT/XLCT
S_2	HOMO-1 → LUMO	0.69	3.32	373	0.0693	368	MLCT/LLCT/XLCT
S_7	HOMO-4 → LUMO HOMO-3 → LUMO	0.58 0.33	4.46	278	0.1262	267	MLCT/XLCT/ILCT

Table S19. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **5**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO → LUMO	0.69	3.32	374	0.0021		MLCT/LLCT/XLCT
S_2	HOMO-1 → LUMO	0.69	3.44	361	0.0795	356	MLCT/LLCT/XLCT
S_4	HOMO-3 → LUMO	0.63	4.35	285	0.0916	283	LLCT/ILCT
S_7	HOMO-4 → LUMO	0.64	4.48	277	0.0636		LLCT/ILCT
S_9	HOMO-1 → LUMO+2	0.59	4.85	255	0.0340	248	MLCT/LLCT/ILCT

Table S20. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **6**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO → LUMO	0.68	3.15	393	0.0025		MLCT/LLCT/XLCT
S_2	HOMO-1 → LUMO	0.67	3.29	377	0.1261	379	MLCT/LLCT/XLCT
S_4	HOMO-3 → LUMO HOMO-2 → LUMO	0.64 -0.22	4.13	300	0.2239	269	MLCT/XLCT/ILCT
S_{10}	HOMO → LUMO+1 HOMO → LUMO+3 HOMO-1 → LUMO+1	0.40 0.39 -0.30	4.49	276	0.0818	251	MLCT/LLCT/XLCT

Table S21. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **7**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO → LUMO	0.70	3.20	387	0.0019		MLCT/LLCT/XLCT
S_2	HOMO-1 → LUMO	0.70	3.33	372	0.0827		MLCT/LLCT/XLCT
S_4	HOMO-3 → LUMO	0.66	4.23	293	0.0996		MLCT/XLCT/ILCT
S_5	HOMO-4 → LUMO HOMO-1 → LUMO+3	0.54 0.27	4.34	286	0.0443		MLCT/LLCT/XLCT/ /ILCT
S_{10}	HOMO-6 → LUMO	0.66	4.74	261	0.0462		ILCT

Table S22. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **8**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO → LUMO	0.69	3.11	399	0.0026		MLCT/LLCT/XLCT
S_2	HOMO-1 → LUMO	0.69	3.24	383	0.1225	381	MLCT/LLCT/XLCT
S_4	HOMO-3 → LUMO	0.63	4.05	306	0.2035	310	MLCT/XLCT/ILCT
S_{10}	HOMO-5 → LUMO	0.65	4.32	287	0.1437	273	MLCT/XLCT/ILCT

Table S23. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **9**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO-1 → LUMO HOMO → LUMO	0.46 0.53	3.70	355	0.0133		MLCT/LLCT/ILCT
S_2	HOMO-1 → LUMO HOMO → LUMO	0.52 0.45	3.86	321	0.1784	324	MLCT/LLCT/ILCT
S_8	HOMO-2 → LUMO+2 HOMO → LUMO+2	0.40 0.40	4.97	250	0.0561	254	MLCT/LLCT/ILCT/ /LXCT
S_9	HOMO-3 → LUMO	0.67	5.12	242	0.1457	233	ILCT

Table S24. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **10**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO-1 → LUMO HOMO → LUMO	0.62 0.32	3.59	346	0.0078		MLCT/LLCT/ILCT
S_2	HOMO-1 → LUMO HOMO → LUMO	0.31 0.60	3.72	333	0.3427	340	MLCT/LLCT/ILCT
S_4	HOMO-3 → LUMO	0.67	4.33	286	0.0975		MLCT/ILCT
S_{10}	HOMO-4 → LUMO HOMO → LUMO+3	0.30 0.24	4.97	250	0.0670	246	MLCT/LLCT/ILCT/ /LXCT

Table S25. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **11**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO → LUMO	0.70	3.64	341	0.1508	346	MLCT/LLCT/XLCT
S_2	HOMO-1 → LUMO	0.70	3.77	329	0.0035		MLCT/LLCT/ILCT
S_8	HOMO-4 → LUMO HOMO-1 → LUMO+2	0.61 0.26	4.85	256	0.0713	260	XLCT/ILCT
S_9	HOMO → LUMO+2 HOMO-1 → LUMO+1	0.52 0.23	4.87	255	0.0727		MLCT/LLCT/LXCT

Table S26. Calculated Excited Energies, Dominant Orbital Excitations, and Oscillator Strength (*f*) from TD-DFT Calculations for Complex **12**

state	excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	*f*	λ_{exp} (nm)	Character
S_1	HOMO → LUMO	0.68	3.38	367	0.0053		MLCT/LLCT/XLCT
S_2	HOMO-2 → LUMO	0.64	3.73	332	0.3409	359	MLCT/LLCT/ILCT
S_6	HOMO → LUMO+1	0.56	4.25	291	0.1982	282	MLCT/LXCT/ILCT

Table S27. Molecular orbital Compositions in the Excited States.

			Contribution (%)			
Complex	Orbital	Energy (eV):	Re:	"sixth" ligand:	CO:	amidino:
1	HOMO	-5.87	46.33	18.86	17.50	17.31
	LUMO	-2.37	5.66	2.43	8.96	82.95
2	HOMO	-5.72	44.18	17.81	18.08	19.93
	LUMO	-2.24	6.12	1.97	9.17	82.74
3	HOMO	-5.76	43.27	17.96	17.58	21.18
	LUMO	-2.40	5.03	2.06	8.16	84.75
4	HOMO	-5.85	42.77	25.28	16.02	15.93
	LUMO	-2.37	5.03	3.41	8.60	82.96
5	HOMO	-5.72	40.88	24.02	16.62	18.48
	LUMO	-2.24	5.49	2.86	8.88	82.77
6	HOMO	-5.76	39.84	24.25	16.03	19.88
	LUMO	-2.40	4.59	2.83	7.85	84.74
7	HOMO	-5.66	39.02	24.30	17.13	19.55
	LUMO	-2.65	5.55	1.69	6.35	86.41
8	HOMO	-5.77	39.68	22.66	16.11	21.56
	LUMO	-2.65	4.86	2.04	6.43	86.67
9	HOMO	-6.61	47.79	3.87	18.38	29.97
	LUMO	-2.78	5.19	0.61	7.48	86.72
10	HOMO	-6.75	41.81	3.31	15.71	39.17
	LUMO	-2.99	4.57	0.59	6.85	87.99
11	HOMO	-6.27	45.69	18.99	18.48	16.83
	LUMO	-3.07	4.44	1.92	5.38	88.26
12	HOMO	-6.60	42.39	13.71	16.14	27.76
	LUMO	-3.01	4.72	1.08	7.41	86.80

Table S28. Calculated Emission Energies and Dominant Orbital Emissions from TD-DFT Calculations.

Complex	state	Excitation	Coef.	E_{calc} (eV)	λ_{calc} (nm)	λ_{exp} (nm)	Character
1	T_1	HOMO → LUMO	0.69	1.88	659	570	^{3}MLCT/^{3}LLCT/^{3}XLCT
2	T_1	HOMO → LUMO	0.69	1.82	682	557	^{3}MLCT/^{3}LLCT/^{3}XLCT
3	T_1	HOMO → LUMO	0.68	1.84	672	559	^{3}MLCT/^{3}LLCT/^{3}XLCT
4	T_1	HOMO → LUMO	0.68	1.91	648	572	^{3}MLCT/^{3}LLCT/^{3}XLCT
5	T_1	HOMO → LUMO	0.68	1.88	661	564	^{3}MLCT/^{3}LLCT/^{3}XLCT
6	T_1	HOMO → LUMO	0.66	1.86	667	581	^{3}MLCT/^{3}LLCT/^{3}XLCT
7	T_1	HOMO → LUMO	0.68	1.48	840		^{3}MLCT/^{3}LLCT/^{3}XLCT
8	T_1	HOMO → LUMO	0.68	1.61	769	606	^{3}MLCT/^{3}LLCT/^{3}XLCT
9	T_1	HOMO → LUMO	0.67	2.07	599	524	^{3}MLCT/^{3}LLCT/^{3}ILCT
10	T_1	HOMO → LUMO	0.66	1.93	644	532	^{3}MLCT/^{3}LLCT/^{3}ILCT
11	T_1	HOMO → LUMO	0.67	1.77	699	536	^{3}MLCT/^{3}LLCT/^{3}XLCT
12	T_1	HOMO → LUMO	0.65	1.90	653	544	^{3}MLCT/^{3}LLCT/^{3}ILCT