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Supporting Information

Luminescent Re(I) Terpyridine Complexes for OLEDs : What does DFT/TD-DFT Probe Reveal?

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Table S1. The optimized ground state geometries of complex **3** obtained using different functionals with LANL2DZ basis set along with the experimental data.

	PBE1PBE	B3LYP	BP86	PBEPBE	B3PW91	M06-2X	Exp*
Bond length (Å)							
Re-C1	1.903	1.913	1.912	1.908	1.906	1.902	1.885
Re-C2	1.920	1.932	1.930	1.926	1.923	1.920	1.920
Re-C3	1.907	1.920	1.919	1.915	1.911	1.908	1.878
Re-Cl	2.496	2.534	2.518	2.513	2.506	2.536	2.482
Re-N1	2.168	2.197	2.178	2.175	2.175	2.221	2.185
Re-N2	2.226	2.267	2.240	2.238	2.236	2.284	2.214
Bond angle (°)							
C1-Re-C2	88.1	88.4	84.5	88.6	87.9	88.9	85.2
N1-Re-N2	74.4	73.9	74.6	74.5	74.4	72.9	74.8

* X-ray data (ref. 26)

Table S2. The optimized ground state geometries of complex **3** 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)	LANL2DZ /6-311+G(d,p)	Exp*
Bond length (Å)					
Re-C1	1.903	1.903	1.904	1.904	1.885
Re-C2	1.920	1.920	1.921	1.921	1.920
Re-C3	1.907	1.905	1.908	1.908	1.878
Re-Cl	2.496	2.504	2.492	2.492	2.482
Re-N1	2.168	2.169	2.175	2174	2.185
Re-N2	2.226	2.222	2.231	2.230	2.214
Bond angle (°)					
C1-Re-C2	88.1	87.4	86.9	87.0	85.2
N1-Re-N2	74.4	74.3	74.1	74.1	74.8

* X-ray data (ref. 26)

Table S3. The calculated lowest-lying absorption results of complex **3** obtained using different functionals with LANL2DZ basis set.

	PBE1PBE	PBEPBE	BPW91	BMK	M11	M05	M06	M06-2X
λ_{cal}	396	561	557	349	308	437	438	336
	B3LYP	B3P86	TPSSLYP1W	wB97XD	M11-L	M05-2X	M06-L	Exp*
λ_{cal}	434	432	537	346	493	332	506	380

* ref. 26

Table S4. TD-DFT calculation on the lowest-lying absorption of complex **3** using PBE1PBE functional with different basis sets.

	LANL2DZ/6-31G(d)	LANL2DZ /6-311G(d)	LANL2DZ /6-311+G(d)	LANL2DZ /6-311+G(d,p)
λ_{cal}	396	393	395	396

Table S5. Calculated emission energies of complexes **1**-**6**.

Complex	$\Delta E_{T_1 - S_0}$ (eV)/(nm)	CIS/nm	TD-DFT/nm	Exp*/nm
1	2.06/602	561.2	565.4	509
2	2.05/604	559.2	573.2	578
3	2.16/573	535.5	541.4	600
4	2.18/570	534.8	541.5	593
5	2.17/572	669.3	649.0	601
6	2.17/572	654.7	634.8	-

* ref. 26

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

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

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	0.141	19.23	32.33	8.34	40.10	p(Re) + π*(CO) + p(Cl) + π*(N^N)
L+4	-0.491	7.43	9.32	0.35	82.90	p(Re) + π*(CO) + π*(N^N)
L+3	-0.750	2.47	1.53	0.53	95.48	π*(N^N)
L+2	-1.385	1.27	1.76	0.47	96.50	π*(N^N)
L+1	-1.696	0.87	0.97	0.36	97.80	π*(N^N)
L	-2.410	4.12	3.98	2.02	89.87	π*(N^N)
H	-5.651	42.87	19.41	33.72	4.00	d(Re) + π(CO) + p(Cl)
H-1	-5.810	39.12	17.19	37.36	6.34	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.380	65.20	27.01	1.47	6.31	d(Re) + π(CO) + π(N^N)
H-3	-7.086	20.01	8.72	58.82	12.45	d(Re) + π(CO) + p(Cl) + π(N^N)
H-4	-7.124	22.28	11.12	55.18	11.41	d(Re) + π(CO) + p(Cl)+π(N^N)
H-5	-7.398	1.21	1.62	2.18	94.99	π(N^N)

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

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	-0.575	5.13	6.06	0.21	88.60	p(Re) + π*(CO) + π*(N^N)
L+4	-0.792	2.27	1.53	0.42	95.78	π*(N^N)
L+3	-1.065	0.02	0.01	0.00	99.96	π*(N^N)
L+2	-1.413	1.37	1.78	0.53	96.32	π*(N^N)
L+1	-1.785	0.76	0.90	0.32	98.02	π*(N^N)
L	-2.441	3.89	3.71	1.91	90.49	π*(N^N)
H	-5.679	43.05	19.64	33.07	4.24	d(Re) + π(CO) + p(Cl)
H-1	-5.819	39.31	17.17	33.88	9.65	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.260	4.31	2.01	6.27	87.41	p(Cl) + π(N^N)
H-3	-6.408	62.18	25.76	1.34	10.72	d(Re) + π(CO) + π(N^N)
H-4	-6.516	0.01	0.00	0.00	99.98	π(N^N)
H-5	-7.114	19.74	8.74	58.91	12.62	d(Re) + π(CO) + p(Cl) + π(N^N)

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

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	-0.577	1.41	0.85	0.26	97.48	π*(N^N)
L+4	-0.591	0.79	0.68	0.07	98.46	π*(N^N)
L+3	-0.797	0.14	0.06	0.00	99.79	π*(N^N)
L+2	-1.173	1.11	1.56	0.40	96.93	π*(N^N)
L+1	-1.424	0.98	0.98	0.42	97.62	π*(N^N)
L	-2.088	3.66	3.48	1.77	91.09	π*(N^N)
H	-5.450	43.03	19.96	32.22	4.79	d(Re) + π(CO) + p(Cl)
H-1	-5.573	39.96	17.62	32.57	9.85	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.138	50.02	21.20	5.24	23.54	d(Re) + π(CO) + π(N^N)
H-3	-6.257	14.77	6.77	11.35	67.11	d(Re) + π(CO) + p(Cl) + π(N^N)
H-4	-6.890	19.85	9.08	59.17	11.90	d(Re) + π(CO) + p(Cl) + π(N^N)
H-5	-6.972	21.05	9.68	48.03	21.24	d(Re) + π(CO) + p(Cl) + π(N^N)

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

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	-0.439	0.75	0.44	0.09	98.71	π*(N^N)
L+4	-0.527	1.98	1.32	0.32	96.38	π*(N^N)
L+3	-0.679	0.13	0.09	0.01	99.76	π*(N^N)
L+2	-1.127	1.02	1.52	0.35	97.12	π*(N^N)
L+1	-1.352	1.00	0.99	0.45	97.57	π*(N^N)
L	-2.034	3.67	3.50	1.77	91.06	π*(N^N)
H	-5.397	42.94	19.87	31.85	5.34	d(Re) + π(CO) + p(Cl)
H-1	-5.522	39.38	17.46	31.58	11.57	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.021	13.88	6.36	11.81	67.95	d(Re) + π(CO) + p(Cl) + π(N^N)
H-3	-6.142	51.53	21.67	3.06	23.73	d(Re) + π(CO) + π(N^N)
H-4	-6.841	19.54	8.74	58.89	12.83	d(Re) + π(CO) + p(Cl) + π(N^N)
H-5	-6.900	21.10	10.06	50.13	18.71	d(Re) + π(CO) + p(Cl) + π(N^N)

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

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	-0.568	1.23	0.90	0.16	97.72	π*(N^N)
L+4	-0.667	0.35	0.36	0.04	99.26	π*(N^N)
L+3	-1.151	1.08	1.46	0.36	97.10	π*(N^N)
L+2	-1.396	1.07	1.00	0.45	97.48	π*(N^N)
L+1	-1.557	0.06	0.11	0.02	99.81	π*(N^N)
L	-2.071	3.64	3.46	1.75	91.15	π*(N^N)
H	-5.432	43.09	19.95	32.18	4.78	d(Re) + π(CO) + p(Cl)
H-1	-5.559	39.98	17.62	32.70	9.69	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.121	48.31	20.47	5.14	26.08	d(Re) + π(CO) + π(N^N)
H-3	-6.229	16.47	7.38	9.46	66.69	d(Re) + π(CO) + p(Cl) + π(N^N)
H-4	-6.769	4.95	2.74	18.15	74.16	d(Re) + p(Cl) + π(N^N)
H-5	-6.881	19.79	9.14	58.55	12.52	d(Re) + π(CO) + p(Cl) + π(N^N)

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

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	-0.596	1.66	1.32	0.21	96.80	π*(N^N)
L+4	-0.768	0.95	0.07	0.01	99.83	π*(N^N)
L+3	-1.160	0.95	1.38	0.27	97.40	π*(N^N)
L+2	-1.278	0.83	0.73	0.36	98.09	π*(N^N)
L+1	-1.573	0.40	0.48	0.18	98.94	π*(N^N)
L	-2.096	3.71	3.54	1.79	90.96	π*(N^N)
H	-5.453	43.05	19.92	32.01	5.02	d(Re) + π(CO) + p(Cl)
H-1	-5.574	39.61	17.46	31.84	11.08	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.078	14.00	6.30	10.48	69.22	d(Re) + π(CO) + p(Cl) + π(N^N)
H-3	-6.189	52.36	22.00	2.46	23.17	d(Re) + π(CO) + π(N^N)
H-4	-6.709	4.10	2.24	15.88	77.78	p(Cl) + π(N^N)
H-5	-6.897	19.89	9.22	58.78	12.10	d(Re) + π(CO) + p(Cl) + π(N^N)

Table S12. Frontier molecular orbital composition (%) in the excited state for complex **1** at the PBE1PBE/LANL2DZ level

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	-0.661	17.81	44.72	6.52	30.95	p(Re) + π*(CO) + π*(N^N)
L+4	-0.826	13.57	31.92	0.46	54.05	p(Re) + π*(CO) + π*(N^N)
L+3	-0.954	6.24	14.55	1.74	77.46	p(Re) + π*(CO) + π*(N^N)
L+2	-1.324	1.17	3.22	0.55	95.07	π*(N^N)
L+1	-1.659	1.68	2.74	1.15	94.43	π*(N^N)
L	-2.840	2.04	2.83	1.26	93.88	π*(N^N)
H	-6.345	51.46	23.54	16.57	16.57	d(Re) + π(CO) + p(Cl) + π(N^N)
H-1	-6.508	49.94	22.26	19.95	7.85	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.822	63.99	28.81	0.71	6.49	d(Re) + π(CO)
H-3	-7.253	0.59	0.50	4.23	94.68	π(N^N)
H-4	-7.511	1.07	1.15	1.01	96.77	π(N^N)
H-5	-7.703	13.83	8.07	61.33	16.76	d(Re) + π(CO) + p(Cl) + π(N^N)

Table S13. Frontier molecular orbital composition (%) in the excited state for complex **2** at the PBE1PBE/LANL2DZ level

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	-0.873	12.04	27.91	0.70	59.35	p(Re) + π*(CO) + π*(N^N)
L+4	-1.010	1.57	3.69	0.33	94.41	π*(N^N)
L+3	-1.032	3.97	9.75	0.82	85.47	π*(CO) + π*(N^N)
L+2	-1.404	1.34	3.45	0.71	94.50	π*(N^N)
L+1	-1.850	1.28	1.96	0.82	95.94	π*(N^N)
L	-2.992	1.91	2.59	1.17	94.34	π*(N^N)
H	-6.223	2.93	1.47	0.54	95.06	π(N^N)
H-1	-6.391	50.25	22.86	16.87	10.01	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.566	32.93	14.60	14.33	38.13	d(Re) + π(CO) + p(Cl) + π(N^N)
H-3	-6.567	19.19	8.52	8.36	63.93	d(Re) + π(CO) + p(Cl) + π(N^N)
H-4	-6.869	64.07	28.63	0.69	6.61	d(Re) + π(CO)
H-5	-7.397	0.64	0.52	5.52	93.32	π(N^N)

Table S14. Frontier molecular orbital composition (%) in the excited state for complex **3** at the PBE1PBE/LANL2DZ level

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	-0.736	4.60	11.51	0.43	83.45	p(Re) + π*(CO) + π*(N^N)
L+4	-0.769	7.89	17.12	0.28	74.70	p(Re) + π*(CO) + π*(N^N)
L+3	-0.903	5.34	12.30	1.53	80.83	p(Re) + π*(CO) + π*(N^N)
L+2	-1.214	0.75	2.70	0.29	96.27	π*(N^N)
L+1	-1.518	1.87	3.38	1.45	93.31	π*(N^N)
L	-2.683	1.61	2.31	1.02	95.06	π*(N^N)
H	-6.218	38.93	18.87	10.37	31.82	d(Re) + π(CO) + p(Cl) + π(N^N)
H-1	-6.327	44.51	19.78	13.99	21.72	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.652	22.19	9.82	14.13	53.86	d(Re) + π(CO) + p(Cl) + π(N^N)
H-3	-6.755	57.85	26.29	1.55	14.31	d(Re) + π(CO) + π(N^N)
H-4	-7.207	0.37	0.33	4.70	94.59	π(N^N)
H-5	-7.445	1.01	1.14	0.93	96.92	π(N^N)

Table S15. Frontier molecular orbital composition (%) in the excited state for complex **4** at the PBE1PBE/LANL2DZ level

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	-0.699	2.09	4.89	0.45	92.57	π*(N^N)
L+4	-0.779	11.72	25.93	0.50	61.86	p(Re) + π*(CO) + π*(N^N)
L+3	-0.935	3.98	8.58	1.40	86.04	π*(CO) + π*(N^N)
L+2	-1.230	0.63	2.62	0.21	96.54	π*(N^N)
L+1	-1.508	1.88	3.50	1.48	93.13	π*(N^N)
L	-2.689	1.59	2.27	1.01	95.13	π*(N^N)
H	-6.207	38.87	18.89	10.65	31.59	d(Re) + π(CO) + p(Cl) + π(N^N)
H-1	-6.319	44.25	19.67	14.58	21.51	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.634	19.59	8.66	13.99	57.77	d(Re) + π(CO) + p(Cl) + π(N^N)
H-3	-6.748	59.98	27.18	1.09	11.75	d(Re) + π(CO) + π(N^N)
H-4	-7.213	0.38	0.34	5.47	93.81	π(N^N)
H-5	-7.413	1.67	1.42	16.22	80.69	p(Cl) + π(N^N)

Table S16. Frontier molecular orbital composition (%) in the excited state for complex **5** at the PBE1PBE/LANL2DZ level

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	-0.778	12.13	28.05	0.43	59.40	p(Re) + π*(CO) + π*(N^N)
L+4	-0.883	4.45	10.45	1.40	83.69	π*(CO) + π*(N^N)
L+3	-1.313	0.72	1.71	0.12	97.45	π*(N^N)
L+2	-1.549	1.02	1.54	0.62	96.83	π*(N^N)
L+1	-1.823	0.11	0.12	0.01	99.76	π*(N^N)
L	-2.268	1.99	3.25	1.45	93.31	π*(N^N)
H	-6.073	11.22	5.82	2.13	80.84	d(Re) + π(N^N)
H-1	-6.277	47.10	21.59	15.48	15.83	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.390	39.54	17.93	14.06	28.47	d(Re) + π(CO) + p(Cl) + π(N^N)
H-3	-6.725	60.64	27.82	1.62	9.92	d(Re) + π(CO) + π(N^N)
H-4	-6.838	7.22	3.38	9.48	79.92	d(Re) + p(Cl) + π(N^N)
H-5	-7.444	1.07	1.18	0.88	96.87	π(N^N)

Table S17. Frontier molecular orbital composition (%) in the excited state for complex **6** at the PBE1PBE/LANL2DZ level

Orbital	Energy (eV)	Contribution (%)				Main bond type
		Re	3CO	Cl	N^N	
L+5	-0.835	4.37	8.48	0.25	86.90	π*(CO) + π*(N^N)
L+4	-0.925	2.61	5.59	0.95	90.84	π*(N^N)
L+3	-1.326	0.61	1.61	0.07	97.71	π*(N^N)
L+2	-1.525	0.98	1.60	0.61	96.81	π*(N^N)
L+1	-1.869	0.08	0.13	0.04	99.75	π*(N^N)
L	-2.262	1.99	3.28	1.44	93.28	π*(N^N)
H	-6.218	39.54	19.22	11.45	29.79	d(Re) + π(CO) + p(Cl) + π(N^N)
H-1	-6.290	26.29	11.76	8.92	53.03	d(Re) + π(CO) + p(Cl) + π(N^N)
H-2	-6.358	32.73	14.73	11.14	41.39	d(Re) + π(CO) + p(Cl) + π(N^N)
H-3	-6.724	61.60	28.21	1.67	8.52	d(Re) + π(CO) + π(N^N)
H-4	-6.884	6.50	3.06	13.54	76.90	d(Re) + p(Cl) + π(N^N)
H-5	-7.502	1.07	0.99	2.33	95.60	π(N^N)

Table S18. Second order perturbation interactions that contribute mainly to the ground state stabilization for complexes **1-6** 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	σ Re 1 - C 29	σ* Re 1 -Cl 2	15.46	0.87	0.104
	σ Re 1 - N 32	π* C 30 - O 36	30.91	0.30	0.090
	n Re 1	σ* Re 1 - C 28	83.78	0.43	0.192
	n Re 1	σ* Re 1 - C 29	49.17	0.48	0.159
	n Re 1	σ* Re 1 - C 30	83.15	0.43	0.191
	n Re 1	π* C 30 - O 36	31.26	0.27	0.094
2	σ Re 1 - C 49	σ* Re 1 -Cl 2	15.32	0.86	0.103
	σ Re 1 - N 52	π* C 50 - O 57	25.99	0.33	0.087
	n Re 1	σ* Re 1 - C 48	78.46	0.44	0.187
	n Re 1	σ* Re 1 - C 49	47.95	0.49	0.158
	n Re 1	σ* Re 1 - C 50	79.42	0.44	0.187
	n Re 1	π* C 50 - O 57	37.14	0.24	0.095
3	σ Re 1 - C 51	σ* Re 1 -Cl 2	15.29	0.86	0.103
	σ Re 1 - N 54	π* C 52 - O 59	27.00	0.33	0.088
	n Re 1	σ* Re 1 - C 50	78.16	0.44	0.187
	n Re 1	σ* Re 1 - C 51	45.56	0.49	0.154
	n Re 1	σ* Re 1 - C 52	77.95	0.44	0.186
	n Re 1	π* C 52 - O 59	39.16	0.24	0.097
4	σ Re 1 - C 49	σ* Re 1 -Cl 2	15.39	0.86	0.103
	σ Re 1 - N 52	π* C 49 - O 56	17.99	0.28	0.066
	n Re 1	σ* Re 1 - C 48	83.68	0.44	0.192
	n Re 1	σ* Re 1 - C 49	48.48	0.49	0.159
	n Re 1	σ* Re 1 - C 50	81.74	0.43	0.189
	n Re 1	π* C 50 - O 57	33.15	0.27	0.095
5	σ Re 1 - C 40	σ* Re 1 -Cl 2	15.29	0.86	0.103
	σ Re 1 - N 43	π* C 41 - O 48	27.07	0.33	0.088
	n Re 1	σ* Re 1 - C 39	78.55	0.44	0.187
	n Re 1	σ* Re 1 - C 40	46.50	0.49	0.156
	n Re 1	σ* Re 1 - C 41	78.24	0.44	0.186
	n Re 1	π* C 41 - O 48	38.60	0.24	0.097
6	σ Re 1 - C 40	σ* Re 1 -Cl 2	15.29	0.86	0.103
	σ Re 1 - N 43	π* C 41 - O 48	27.19	0.32	0.088
	n Re 1	σ* Re 1 - C 39	78.59	0.44	0.187
	n Re 1	σ* Re 1 - C 40	46.49	0.49	0.156
	n Re 1	σ* Re 1 - C 41	78.34	0.44	0.186
	n Re 1	π* C 41 - O 48	38.34	0.24	0.097

Table S19. Topological properties at the BCPs in Re-CO, ReCl and Re-N 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	0.1516	-0.1351	0.2013	-0.0662	0.0693	0.2675	-1.3289
2	0.1522	-0.1332	0.2001	-0.0669	0.0744	0.2671	-1.3348
3	0.1523	-0.1338	0.2009	-0.0671	0.0754	0.2679	-1.3335
4	0.1516	-0.1357	0.2018	-0.0661	0.0658	0.2679	-1.3276
5	0.1523	-0.1336	0.2007	-0.0671	0.0751	0.2678	-1.3343
6	0.1522	-0.1337	0.2007	-0.0670	0.0756	0.2678	-1.3343
Re-CO(2) BCP							
1	0.1457	-0.1327	0.1935	-0.0608	0.1074	0.2543	-1.3142
2	0.1457	-0.1324	0.1932	-0.0609	0.1077	0.2541	-1.3152
3	o.1461	-0.1329	0.1941	-0.0611	0.1014	0.2552	-1.3148
4	0.1462	-0.1329	0.1942	-0.0612	0.1012	0.2554	-1.3151
5	0.1462	-0.1326	0.1939	-0.0612	0.1007	0.2551	-1.3156
6	0.1462	-0.1328	0.1940	-0.0612	0.1014	0.2553	-1.3160
Re- CO(3) BCP							
1	0.1501	-0.1349	0.2003	-0.0654	0.0538	0.2658	-1.327
2	0.1503	-0.1347	0.2004	-0.0657	0.0478	0.2661	-1.3278
3	0.1507	-0.1350	0.2011	-0.0660	0.0451	0.2671	-1.3282
4	0.1508	-0.1348	0.2009	-0.0661	0.0490	0.2671	-1.3295
5	0.1508	-0.1352	0.2013	-0.0661	0.0457	0.2674	-1.3284
6	0.1507	-0.1351	0.2011	-0.0659	0.0452	0.2671	-1.3282
Re- Cl BCP							
1	0.0613	-0.0484	0.0599	-0.0115	0.0314	0.0715	-1.1937
2	0.0611	-0.0482	0.0597	-0.0114	0.0322	0.0712	-1.1926
3	0.0605	-0.0479	0.0591	-0.0112	0.0312	0.0703	-1.1895
4	0.0606	-0.0479	0.0592	-0.0112	0.0333	0.0704	-1.1892
5	0.0605	-0.0481	0.0592	-0.0112	0.0313	0.0705	-1.1909
6	0.0604	-0.0480	0.0592	-0.0111	0.0311	0.0703	-1.1875
Re-N(1) BCP							
1	0.0827	-0.0979	0.1084	-0.0105	0.1437	0.1189	-1.0969
2	0.0821	-0.0973	0.1076	-0.0103	0.1462	0.1179	-1.0957
3	0.0816	-0.0965	0.1066	-0.0100	0.1501	0.1166	-1.0938
4	0.0818	-0.0967	0.1068	-0.0101	0.1476	0.1170	-1.0955
5	0.0817	-0.0964	0.1065	-0.0102	0.1526	0.1167	-1.0958
6	0.0816	-0.0964	0.1065	-0.0101	0.1517	0.1166	-1.0948
Re-N(2) BCP							
1	0.0712	-0.0782	0.0861	-0.0079	0.2415	0.0940	-1.0918
2	0.0717	-0.0788	0.0863	-0.0080	0.2335	0.0949	-1.0997
3	0.0721	-0.0784	0.0866	-0.0082	0.2309	0.0948	-1.0947
4	0.0722	-0.0786	0.0868	-0.0082	0.2347	0.0951	-1.0956
5	0.0722	-0.0786	0.0868	-0.0083	0.2287	0.0951	-1.0956
6	0.0723	-0.0789	0.0871	-0.0083	0.2294	0.0954	-1.0953

Table S20. Selected bond parameters for complexes 1-7 in the low lying triplet excited state at the DFT, TDDFT and CIS methods.

Bond Parameters	1			2			3			4			5			6		
	DFT	TDDFT	CIS	DFT	TDDFT	CIS	DFT	TDDFT	CIS	DFT	TDDFT	CIS	DFT	TDDFT	CIS	DFT	TDDFT	CIS
Re-C1(Å)	1.955	1.947	1.942	1.955	1.960	1.943	1.964	1.932	1.941	1.966	1.917	1.941	1.962	1.903	1.939	1.964	1.903	1.939
Re-C2(Å)	1.960	1.952	1.957	1.959	1.935	1.957	1.941	1.922	1.957	1.935	1.919	1.957	1.946	1.919	1.955	1.941	1.919	1.955
Re-C3(Å)	1.967	1.954	1.926	1.967	1.949	1.926	1.960	1.910	1.925	1.954	1.900	1.924	1.962	1.900	1.924	1.960	1.900	1.924
Re-Cl(Å)	2.412	2.442	2.622	2.401	2.447	2.619	2.412	2.528	2.626	2.427	2.545	2.626	2.415	2.524	2.623	2.416	2.526	2.624
Re-N1(Å)	2.131	2.125	2.183	2.131	2.145	2.183	2.140	2.163	2.180	2.146	2.165	2.180	2.136	2.171	2.190	2.139	2.172	2.190
Re-N2(Å)	2.134	2.135	2.241	2.134	2.109	2.241	2.112	2.128	2.236	2.104	2.159	2.236	2.117	2.219	2.244	2.113	2.219	2.243
C1-Re-C2(°)	83.7	83.6	87.9	83.7	85.0	87.8	85.2	88.1	87.9	86.7	88.1	87.8	84.6	87.8	87.8	85.2	87.8	87.8
N1-Re-N2(°)	76.5	77.2	75.5	76.6	77.4	75.5	77.1	76.8	75.4	77.3	76.2	75.5	77.0	74.7	74.6	77.1	74.6	74.6

Figure S1. Molecular graph of the complexes **1-6**. All critical points are shown, as attractors by greater circles: BCPs, small red circles; RCPs, yellow ones. The bond paths are also shown.

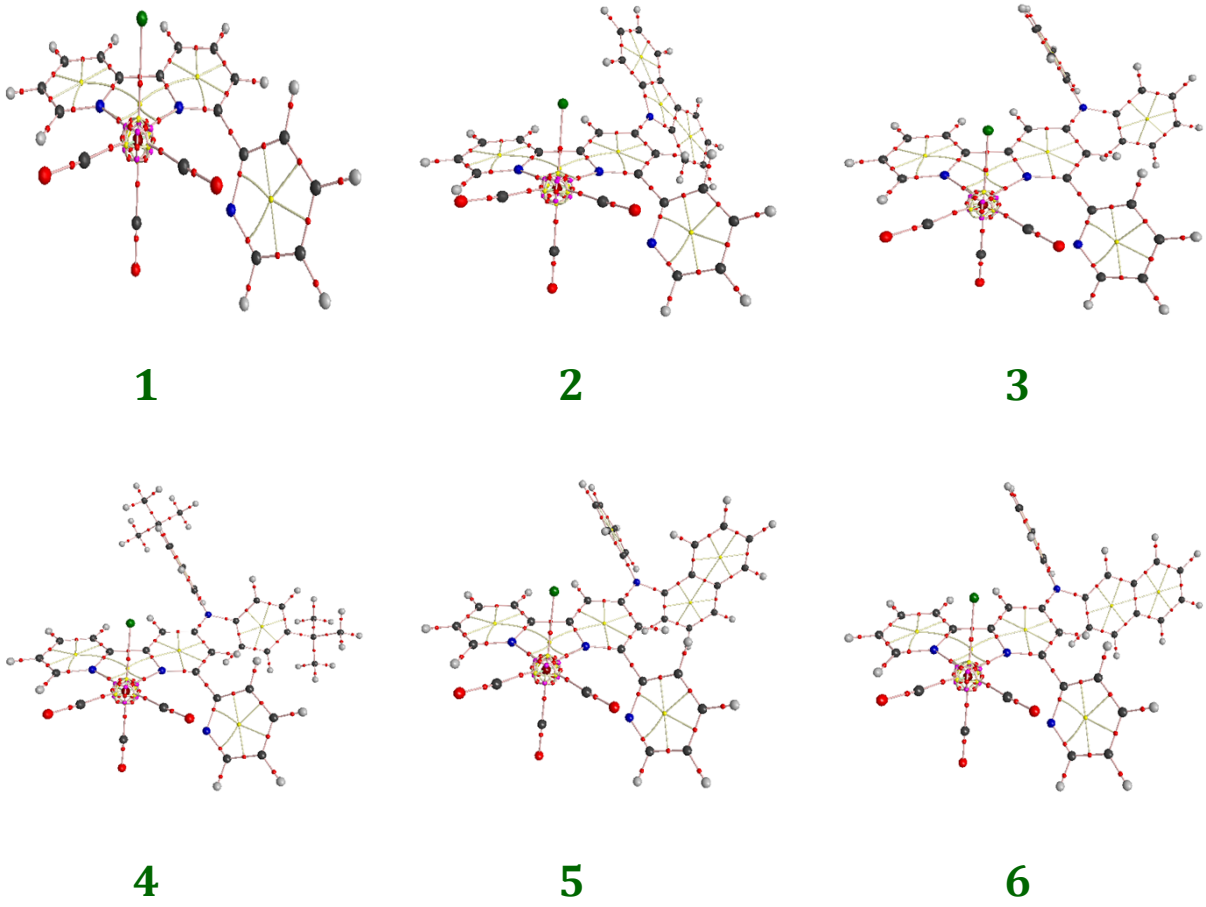


Figure S2. Effect of Solvent on Absorption Spectra of Complexes **1-6** computed at PBE1PBE/LANL2DZ level.

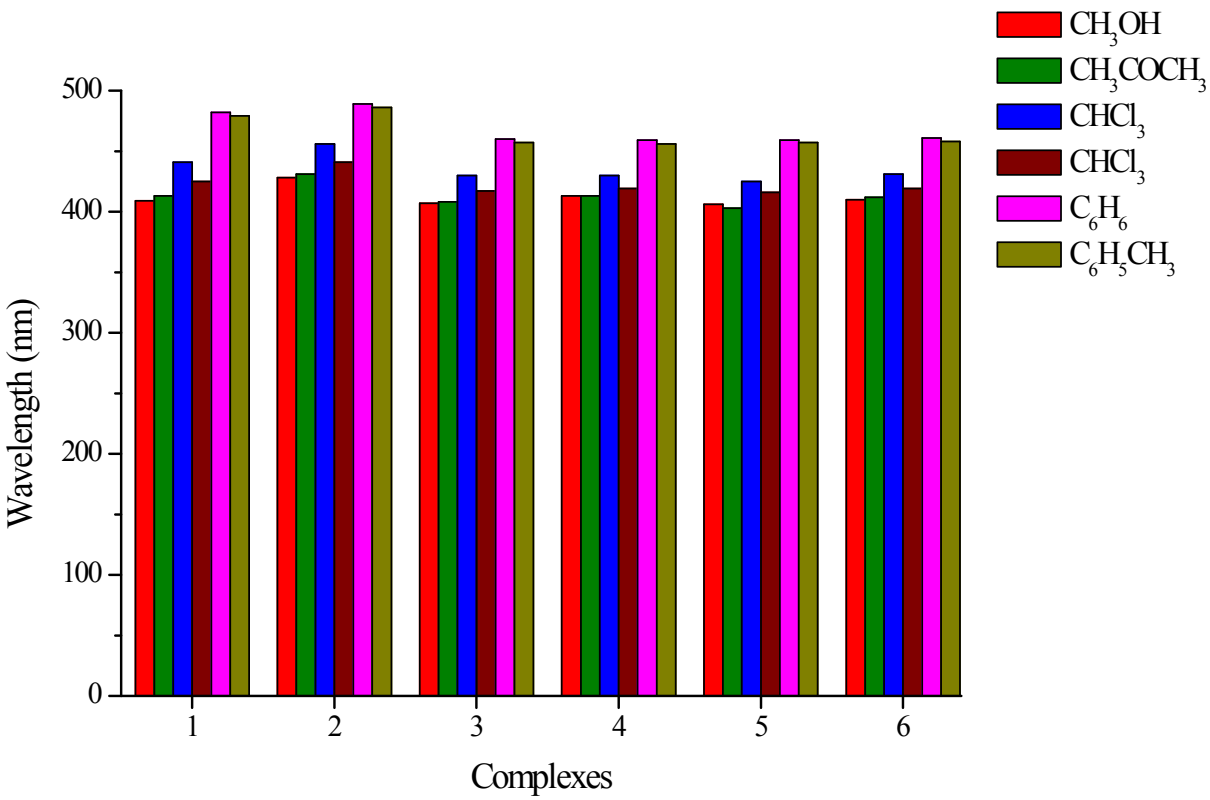


Figure S3. Effect of Solvent on Phosphorescence Spectra of Complexes **1-6** computed at PBE1PBE/LANL2DZ level.

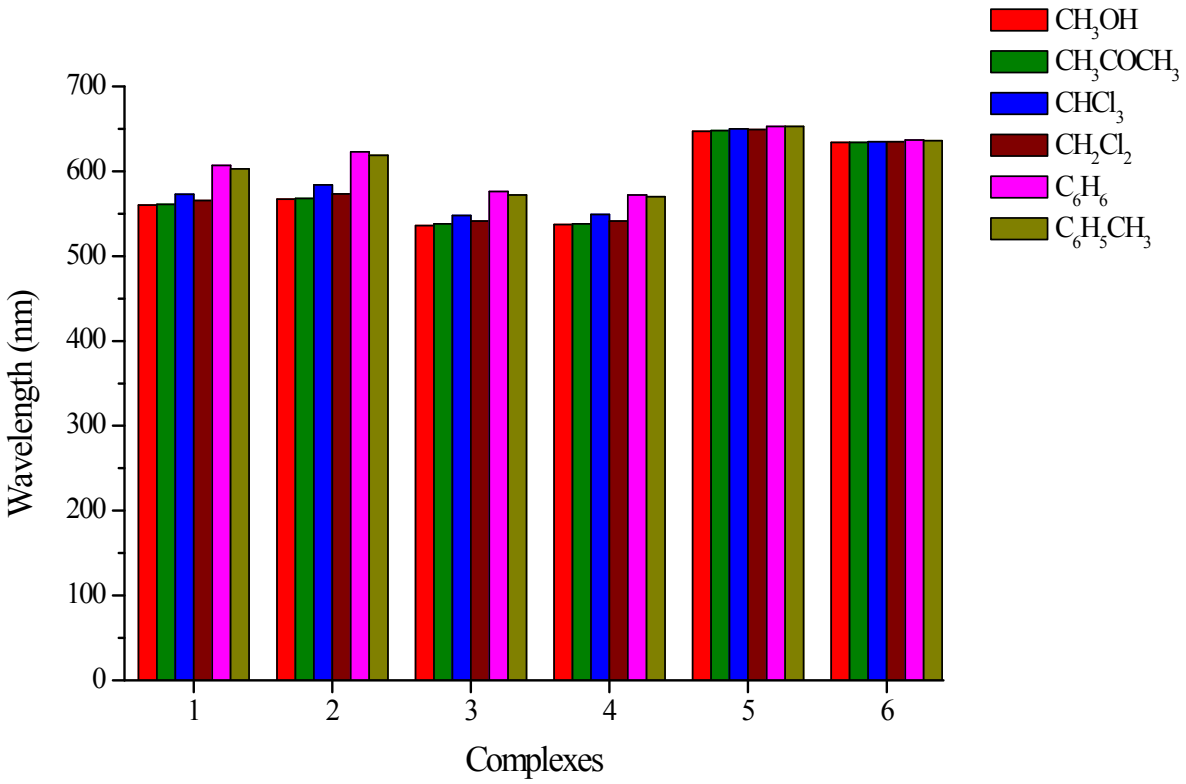


Figure S4. Natural Transition Orbitals (NTOs) for the Complex **3** and **4** illustrating the nature of optically active singlet excited states in the absorption bands. Shown are only occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 50% to each excited state. All transitions have mixed ^{1}MLCT/^{1}LLCT/^{1}ILCT character.

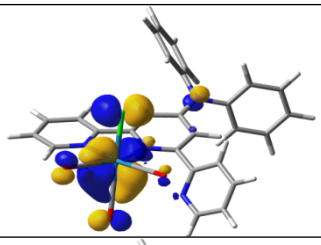
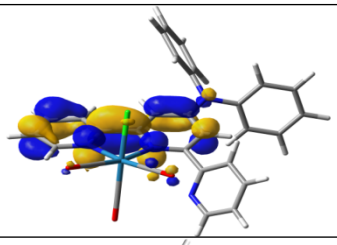
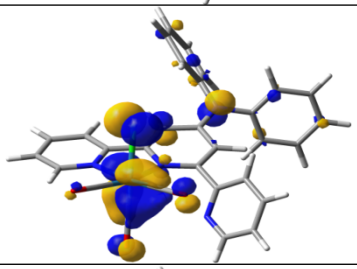
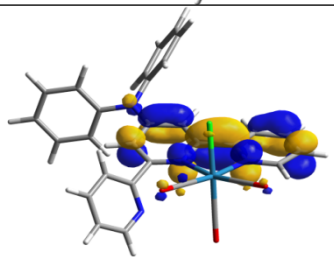
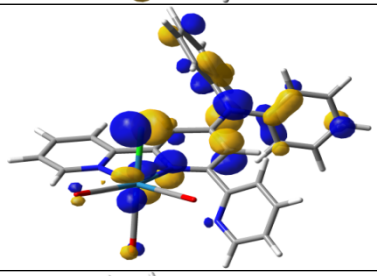
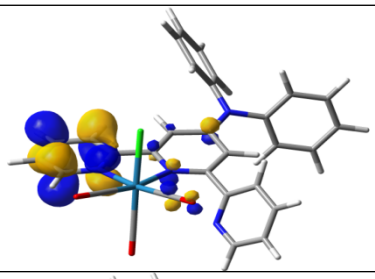
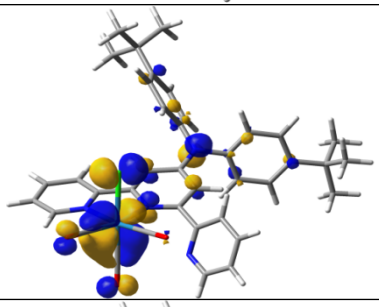
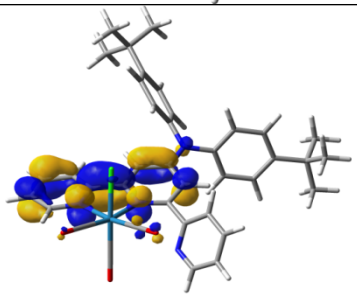
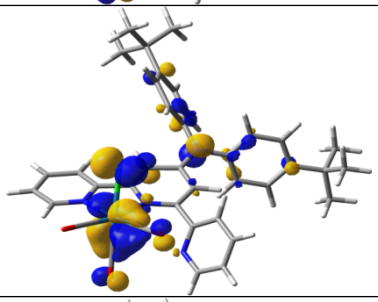
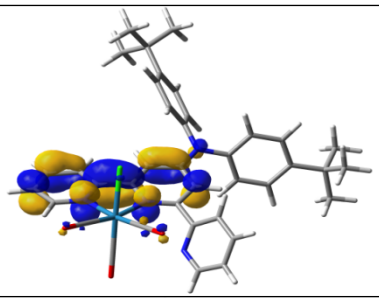
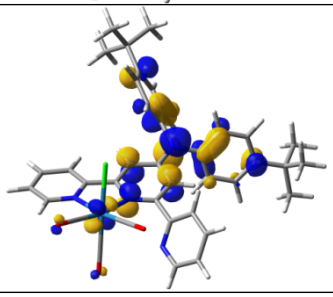
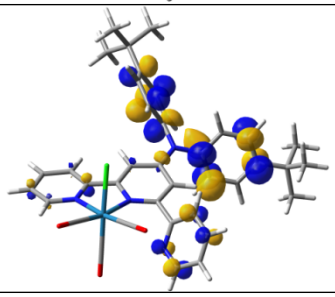
Complex	λ_{cal} (nm)		Hole	Electron
3	395.6	S_2 W=0.99		
	282.9	S_{14} W=0.98		
	243.5	S_{37} W=0.57		
4	400.6	S_2 W=0.99		
	273.3	S_{20} W=0.98		
	246.3	S_{36} W=0.74		

Figure S5. 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 40% to each excited state. All transitions have mixed ^{1}MLCT/^{1}LLCT/^{1}ILCT character.

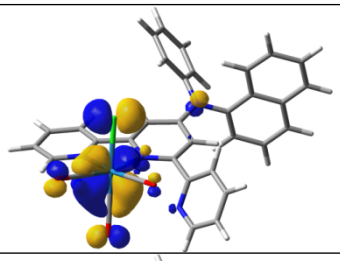
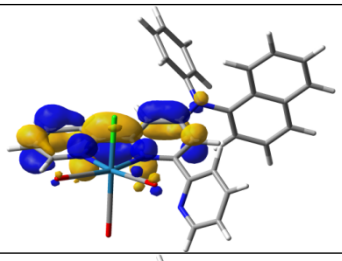
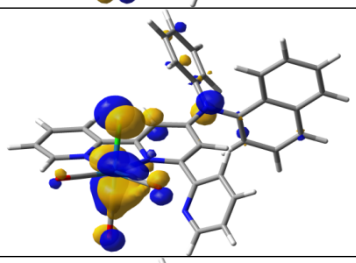
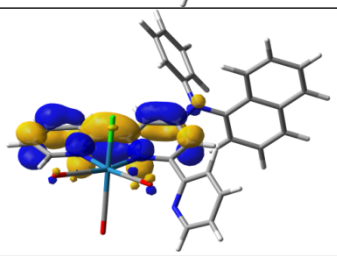
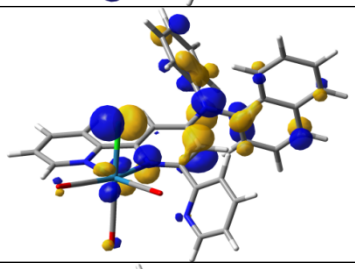
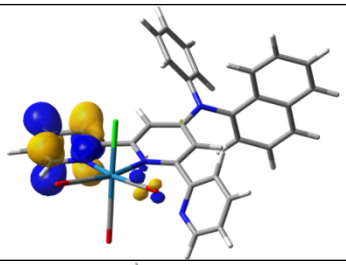
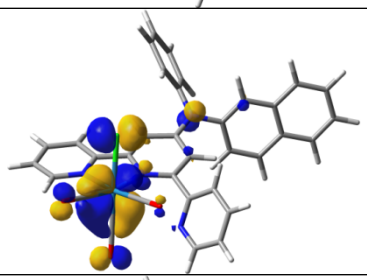
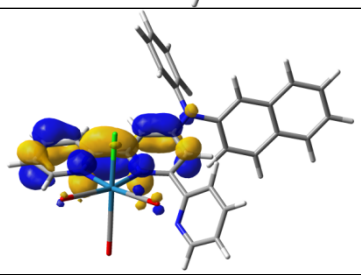
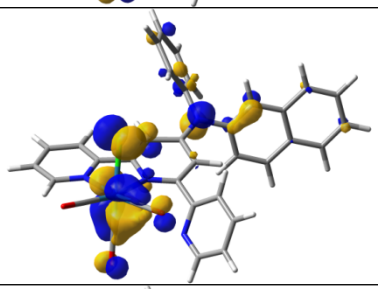
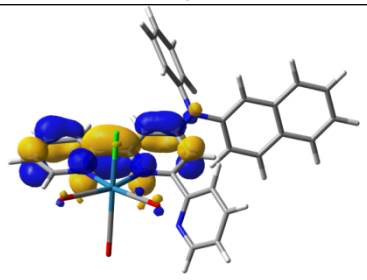
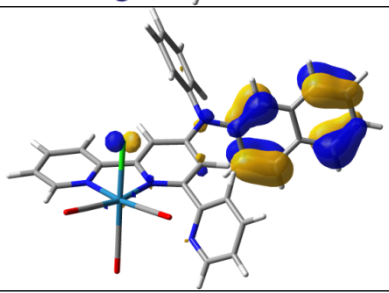
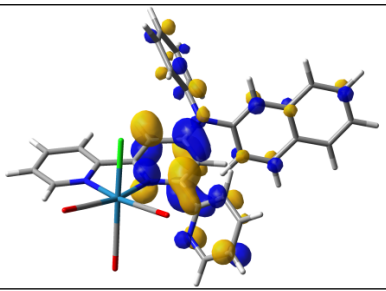
Complex	λ_{cal} (nm)		Hole	Electron
5	394.5	S_2 W=0.99		
	282.9	S_{17} W=0.98		
	247.1	S_{40} W=0.50		
6	399.9	S_2 W=0.99		
	275.9	S_{20} W=0.98		
	247.9	S_{30} W=0.46		

Figure S6. The calculated lowest-lying absorption results of complex **3** obtained using different functionals along with the experimental results.

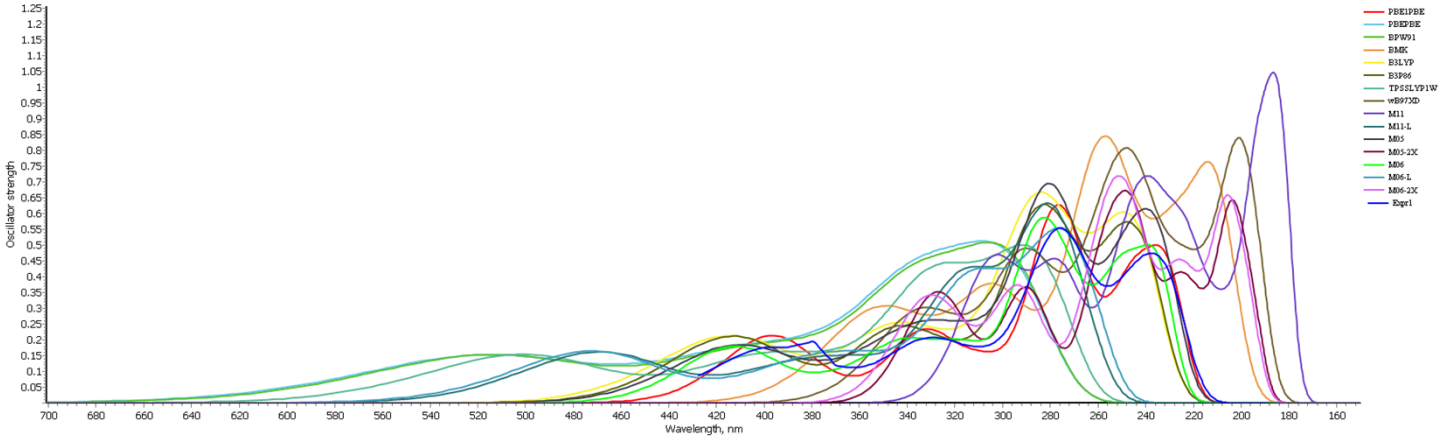


Figure S7. TD-DFT calculation on the lowest-lying absorption of complex **3** using PBE1PBE functional with different basis sets.