

Supporting Information

Luminescence property of some monomeric and dimeric cycloplatinated(II) complexes containing biphosphine ligands

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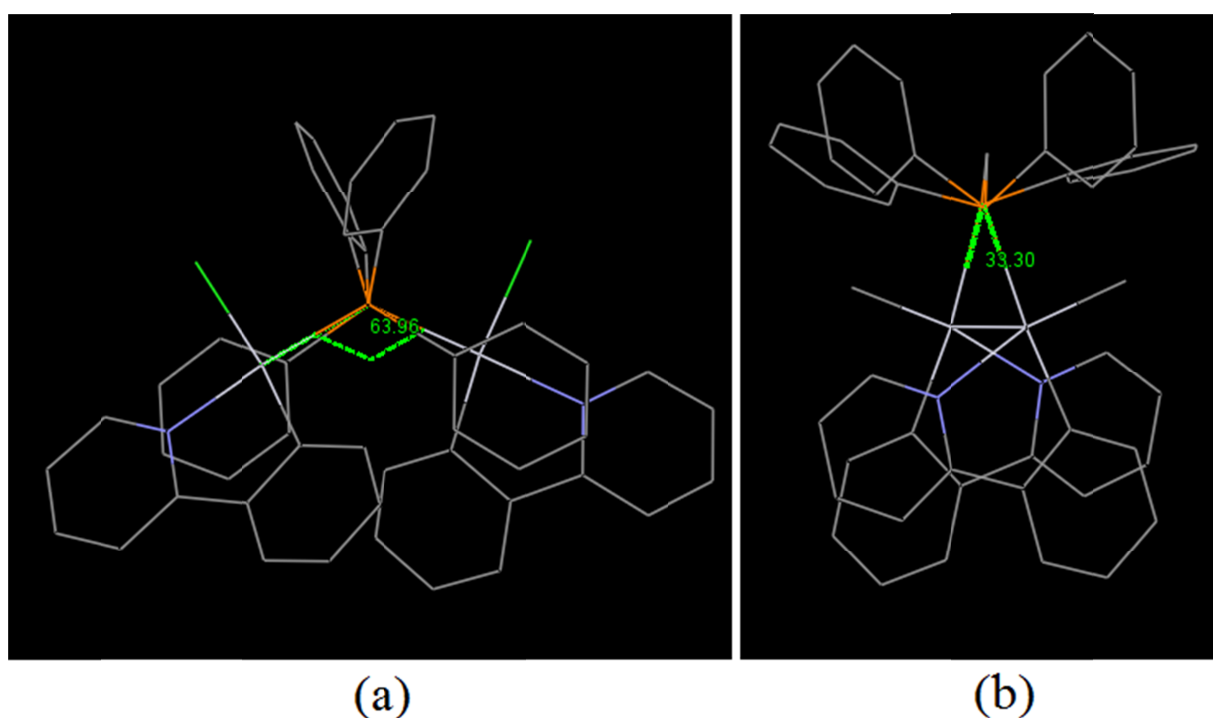


Figure S1. (a) Pt-P-Pt torsion angle (63.9°) view of complex **5d**. (b) Pt-P-Pt torsion angle (33.3°) view of dimer complex containing methyl ligands instead of chloro ligands which was synthesized by Jamali and coworkers (*Dalton Trans.*, 2011, **40**, 9123-9130).

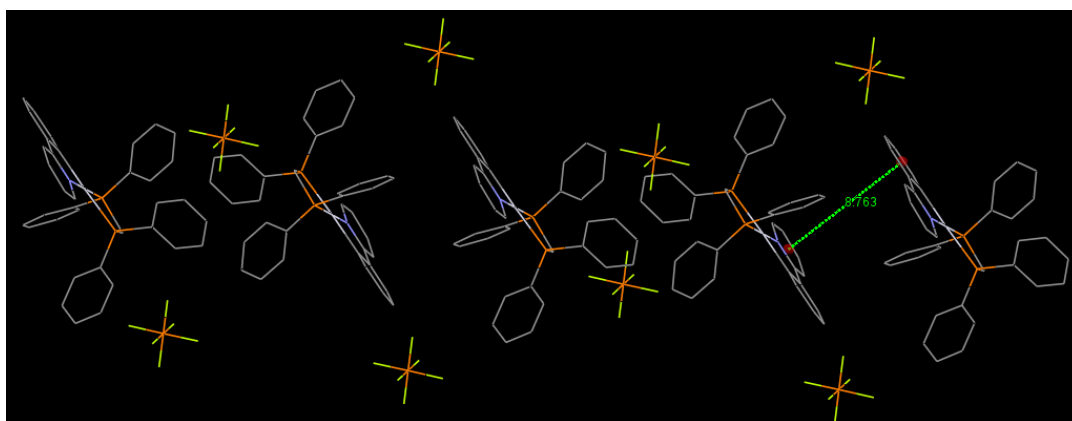


Figure S2. Crystal packing of $[\text{Pt}(\text{ppy})(\text{dppm})]\text{PF}_6$ complex which was reported by Rillema and coworkers (J. DePriest, G. Y. Zheng, N. Goswami, D. M. Eichhorn, C. Woods and D. P. Rillema, *Inorg. Chem.* 2000, **39**, 1955-1963). CIF file has been downloaded from Cambridge Crystallographic Database Center website.

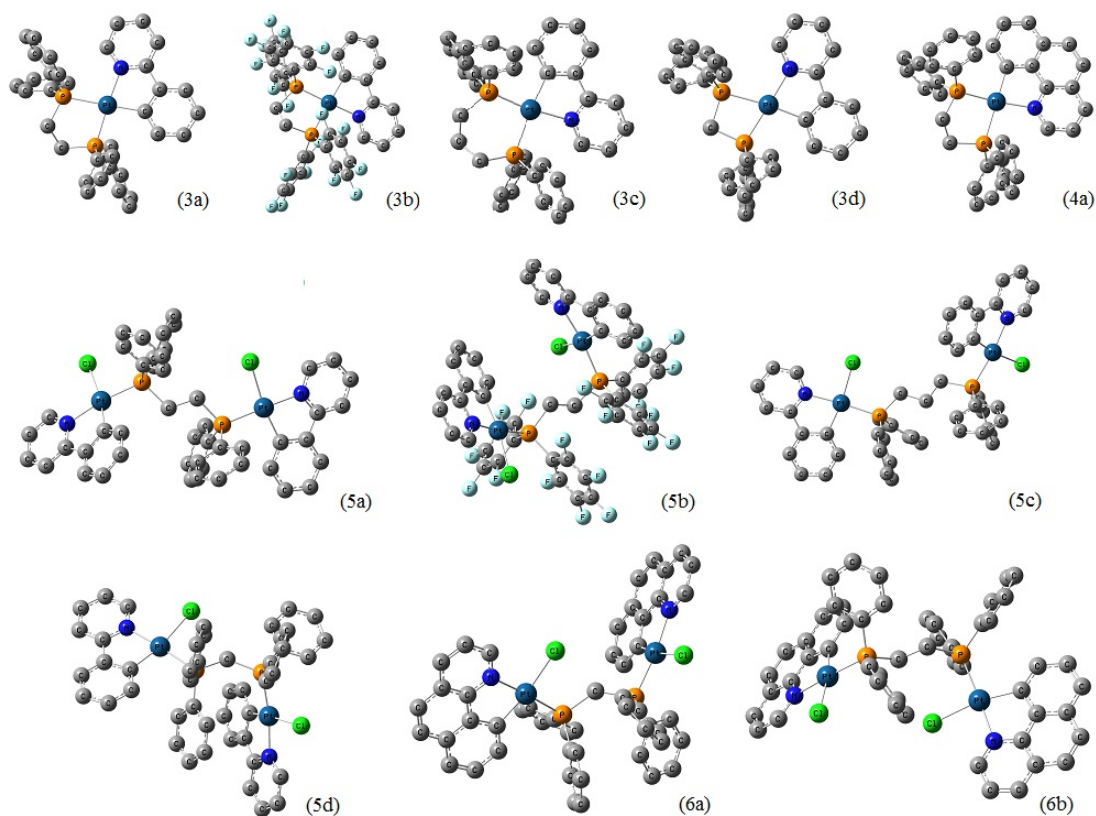


Figure S3. Optimized structures of all the studied complexes in dichloromethane solvent.

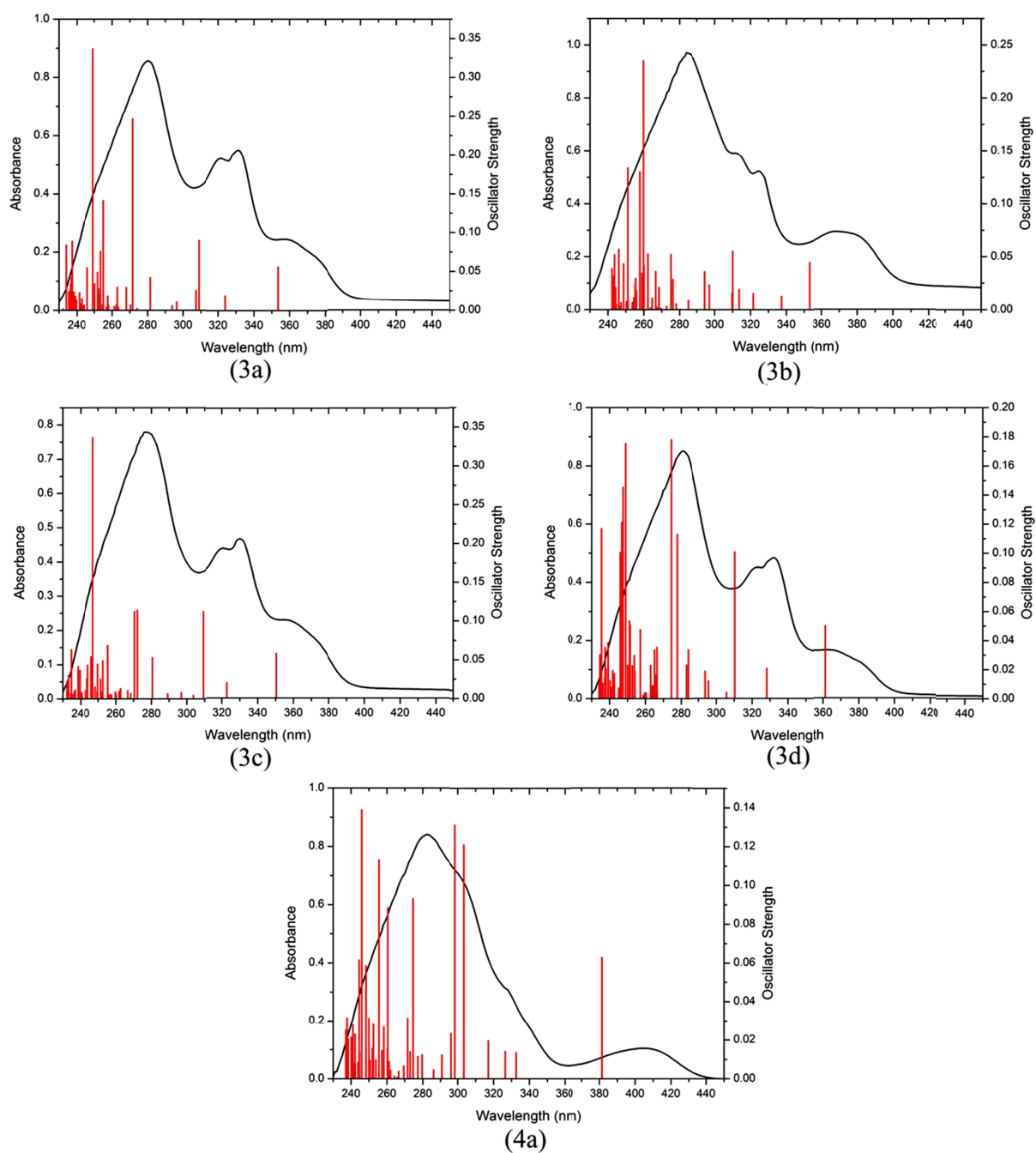


Figure S4. Overlaid experimental absorbance (spectra) and calculated TDDFT (bars) for the monomeric complexes

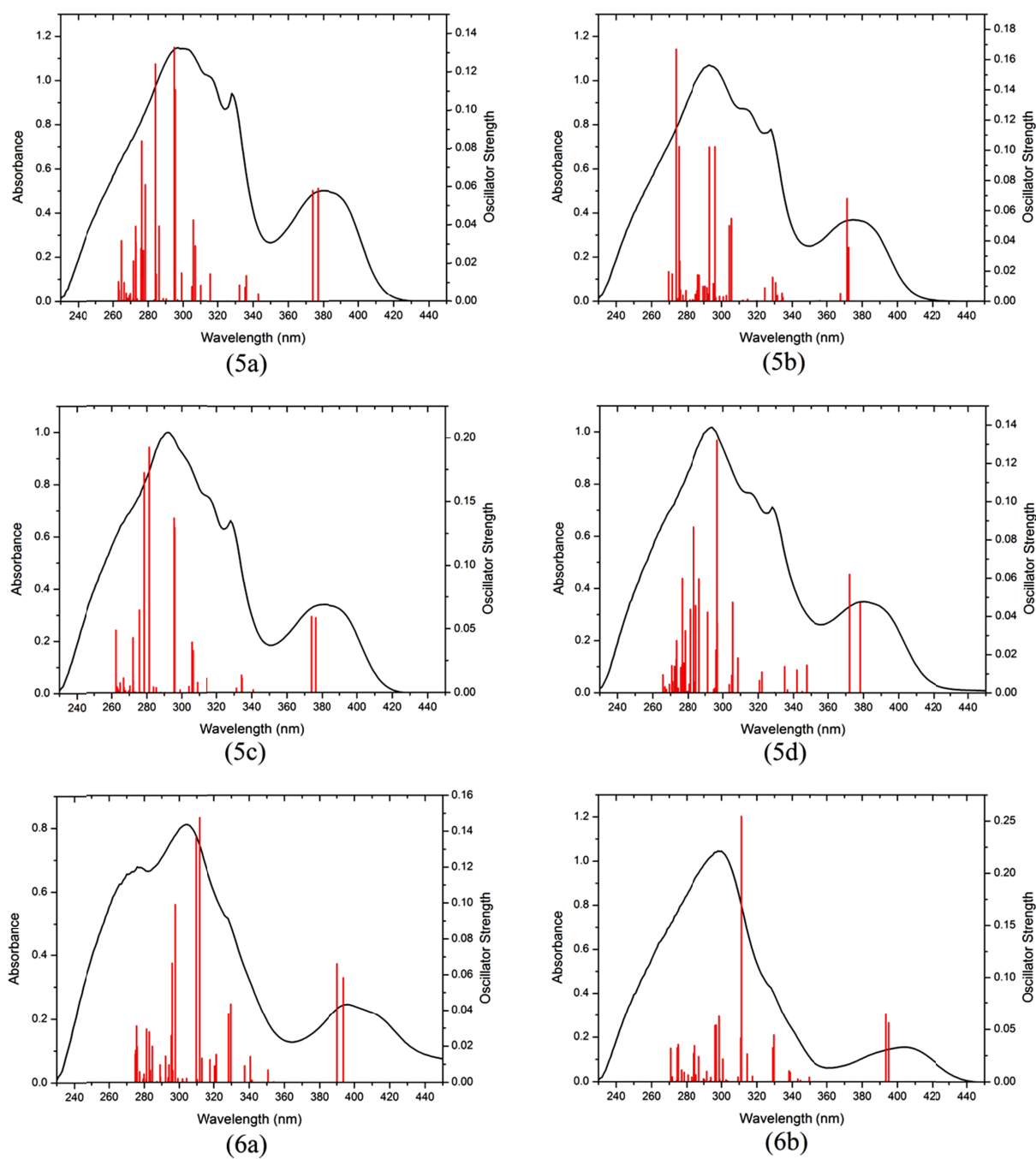
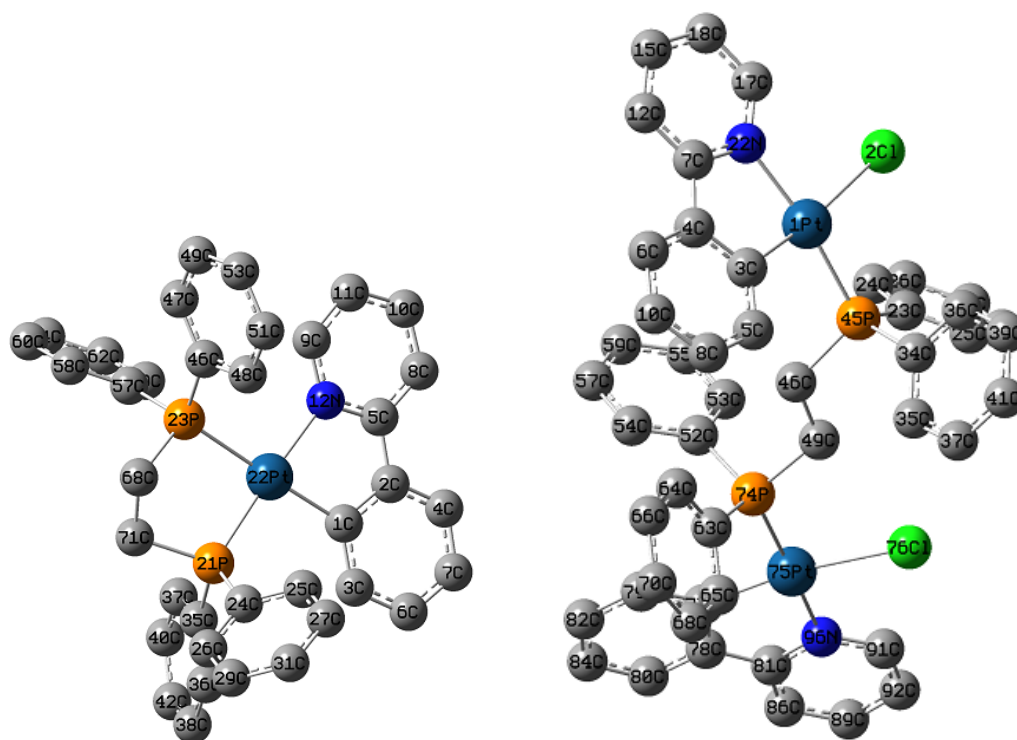


Figure S5. Overlaid experimental absorbance (spectra) and calculated TDDFT (bars) for the dimeric complexes



Atom numbering of the monomeric and dimeric complexes for Tables S1-S4.

Table S1. Selected calculated bond distances (Å) and angles (deg) for the monomer complexes (optimized in dichloromethane) compared to the experimental data of the complex **3a**.

Bond distance or angle	3a (S ₀)	3a (expt.)	3b (S ₀)	3c (S ₀)	3d (S ₀)	4a (S ₀)
Pt22-P23	2.434	2.303	2.438	2.455	2.451	2.427
Pt22-P21	2.311	2.243	2.299	2.325	2.308	2.302
Pt22-N12	2.137	2.074	2.121	2.160	2.123	2.150
Pt22-C1	2.060	2.059	2.050	2.074	2.042	2.066
P23-C46	1.836	1.814	1.839	1.842	1.834	1.833
P23-C57	1.833	1.814	1.844	1.844	1.829	1.839
P21-C24	1.832	1.800	1.843	1.844	1.825	1.836
P21-C35	1.834	1.809	1.838	1.841	1.830	1.832
N12-Pt22-C1	79.66	79.73	80.04	79.06	79.99	80.24
P23-Pt22-P21	84.40	84.45	84.20	92.83	72.87	85.50
N12-Pt22-P23	98.94	98.61	99.39	94.85	105.82	98.64
C1-Pt22-P21	96.99	98.20	96.85	93.361	101.57	96.60
Pt22-N12-C5	114.46	115.93	114.42	114.34	114.55	112.54
Pt22-C1-C2	113.87	113.49	113.68	114.07	114.00	112.25
Pt22-P23-C68	105.44	106.68	105.90	118.05	92.11	105.73
Pt22-P21-C71	108.21	109.09	108.57	119.95	97.08	108.17
N12-Pt22-P21	176.64	173.33	173.58	172.13	176.37	171.80
C1-Pt22-P23	178.15	170.56	174.73	173.00	172.81	172.10
Bond distance or angle	3a (T ₁)	-	3b (T ₁)	3c (T ₁)	3d (T ₁)	4a (T ₁)
Pt22-P23	2.439	-	2.454	2.457	2.453	2.422
Pt22-P21	2.321	-	2.304	2.334	2.320	2.310
Pt22-N12	2.100	-	2.091	2.122	2.081	2.129
Pt22-C1	2.027	-	2.020	2.037	2.008	2.061
P23-C46	1.836	-	1.843	1.842	1.834	1.833
P23-C57	1.834	-	1.851	1.845	1.829	1.839
P21-C24	1.834	-	1.840	1.846	1.826	1.837
P21-C35	1.835	-	1.844	1.842	1.832	1.832
N12-Pt22-C1	80.72	-	80.32	79.79	81.07	79.80
P23-Pt22-P21	84.14	-	84.39	92.84	72.64	85.31
N12-Pt22-P23	98.01	-	99.73	94.33	105.14	98.81
C1-Pt22-P21	97.12	-	95.54	93.22	101.44	97.25
Pt22-N12-C5	114.17	-	113.99	113.81	114.43	113.31
Pt22-C1-C2	112.93	-	112.80	112.92	113.13	112.81
Pt22-P23-C68	105.87	-	106.67	118.16	92.33	106.06
Pt22-P21-C71	107.80	-	108.60	119.17	96.95	107.95
N12-Pt22-P21	177.65	-	171.68	172.29	175.77	172.67
C1-Pt22-P23	178.71	-	179.93	172.94	172.22	169.34

Table S2. Selected calculated bond distances (Å) and angles (deg) for the dimer complexes (optimized in dichloromethane).

Bond distance or angle	5a (S ₀)	5b (S ₀)	5c (S ₀)	5d (S ₀)	6a (S ₀)	6b (S ₀)
Pt1-Cl2	2.517	2.528	2.520	2.519	2.524	2.500
Pt1-N22	2.131	2.105	2.131	2.129	2.141	2.143
Pt1-C3	2.021	2.021	2.024	2.026	2.033	2.033
Pt1-P45	2.312	2.312	2.318	2.314	2.327	2.310
P45-C23	1.839	1.860	1.839	1.845	1.840	1.842
P45-C34	1.834	1.850	1.845	1.846	1.841	1.842
P45-C46	1.872	1.850	1.864	1.871	1.888	1.867
Cl2-Pt1-N22	92.06	93.75	91.40	91.46	89.14	90.46
Cl2-Pt1-P45	92.37	84.51	91.75	93.27	94.16	92.70
N22-Pt1-C3	79.81	79.98	79.99	79.79	80.69	80.63
C3-Pt1-P45	96.84	102.57	96.86	96.74	95.99	96.33
Pt1-N22-C7	114.12	114.70	114.39	114.28	112.46	112.43
Pt1-C3-C4	114.36	114.14	114.26	114.26	112.45	112.50
Pt1-P45-C46	110.28	112.54	113.93	116.71	111.70	107.42
N22-Pt1-P45	170.49	171.93	175.92	171.60	176.55	173.90
Cl2-Pt1-C3	168.66	170.92	171.37	166.24	169.82	170.89
Bond distance or angle	5a (T ₁)	5b (T ₁)	5c (T ₁)	5d (T ₁)	6a (T ₁)	6b (T ₁)
Pt1-Cl2	2.517	2.537	2.513	2.510	2.501	2.502
Pt1-N22	2.131	2.107	2.098	2.104	2.127	2.143
Pt1-C3	2.021	2.020	1.984	1.981	2.017	2.033
Pt1-P45	2.312	2.311	2.339	2.334	2.345	2.315
P45-C23	1.839	1.858	1.839	1.842	1.840	1.842
P45-C34	1.834	1.846	1.845	1.846	1.842	1.839
P45-C46	1.872	1.874	1.863	1.868	1.887	1.873
Cl2-Pt1-N22	92.03	93.19	90.95	91.41	89.89	90.23
Cl2-Pt1-P45	92.46	83.99	91.15	92.25	93.37	91.95
N22-Pt1-C3	79.81	79.96	81.39	80.93	80.26	80.60
C3-Pt1-P45	96.77	104.10	96.57	97.06	96.45	97.47
Pt1-N22-C7	114.14	114.67	113.76	113.61	112.88	112.45
Pt1-C3-C4	114.36	114.20	113.06	112.91	113.39	112.45
Pt1-P45-C46	110.31	112.25	113.73	117.39	112.12	109.25
N22-Pt1-P45	170.46	171.44	175.91	173.21	176.46	173.87
Cl2-Pt1-C3	168.72	168.14	172.18	162.27	170.15	170.33

Table S3. Selected calculated bond distances (Å) and angles (deg) for the monomer complexes (optimized in solid state) compared to the experimental data of complex **3a**.

Bond distance or angle	3a (S ₀)	3a (exptl)	3b (S ₀)	3c (S ₀)	3d (S ₀)	4a (S ₀)
Pt22-P23	2.433	2.303	2.432	2.457	2.445	2.422
Pt22-P21	2.311	2.243	2.298	2.326	2.307	2.303
Pt22-N12	2.135	2.074	2.119	2.158	2.117	2.146
Pt22-C1	2.059	2.059	2.050	2.072	2.040	2.062
P23-C46	1.835	1.814	1.838	1.841	1.833	1.832
P23-C57	1.832	1.814	1.843	1.844	1.827	1.837
P21-C24	1.832	1.800	1.840	1.841	1.824	1.834
P21-C35	1.831	1.809	1.835	1.840	1.828	1.831
N12-Pt22-C1	79.74	79.73	80.08	79.14	80.16	80.34
P23-Pt22-P21	84.64	84.45	84.38	93.26	73.23	85.83
N12-Pt22-P23	98.71	98.61	99.35	94.75	105.55	98.53
C1-Pt22-P21	96.90	98.20	96.68	93.07	101.31	96.41
Pt22-N12-C5	114.30	115.93	114.31	114.16	114.41	112.47
Pt22-C1-C2	113.76	113.49	113.64	114.01	113.92	112.19
Pt22-P23-C68	105.55	106.68	105.97	118.03	91.99	105.53
Pt22-P21-C71	107.77	109.09	108.47	119.11	96.73	107.68
N12-Pt22-P21	176.53	173.33	173.63	171.59	175.69	171.44
C1-Pt22-P23	178.43	170.56	174.43	172.07	173.29	171.38
Bond distance or angle	3a (T ₁)	-	3b (T ₁)	3c (T ₁)	3d (T ₁)	4a (T ₁)
Pt22-P23	2.433	-	2.431	2.453	2.443	2.418
Pt22-P21	2.322	-	2.308	2.334	2.319	2.310
Pt22-N12	2.095	-	2.080	2.121	2.074	2.120
Pt22-C1	2.028	-	2.021	2.036	2.007	2.061
P23-C46	1.836	-	1.839	1.842	1.833	1.831
P23-C57	1.833	-	1.844	1.844	1.827	1.836
P21-C24	1.833	-	1.841	1.844	1.826	1.835
P21-C35	1.833	-	1.838	1.841	1.829	1.832
N12-Pt22-C1	80.71	-	80.92	79.73	81.15	79.92
P23-Pt22-P21	84.46	-	84.13	93.00	73.03	85.60
N12-Pt22-P23	97.98	-	98.67	94.62	104.73	98.57
C1-Pt22-P21	96.83	-	96.81	92.93	101.46	97.19
Pt22-N12-C5	114.33	-	114.48	113.85	114.57	113.41
Pt22-C1-C2	112.95	-	112.90	112.96	113.09	112.68
Pt22-P23-C68	105.73	-	106.15	117.91	92.30	105.69
Pt22-P21-C71	107.56	-	108.44	118.73	96.55	107.68
N12-Pt22-P21	177.54	-	174.24	171.82	174.97	171.79
C1-Pt22-P23	178.68	-	173.93	172.13	172.46	169.85

Table S4. Selected calculated bond distances (Å) and angles (deg) for the dimer complexes (optimized in solid state).

Bond distance or angle	5a (S ₀)	5b (S ₀)	5c (S ₀)	5d (S ₀)	6a (S ₀)	6b (S ₀)
Pt1-Cl2	2.471	2.478	2.513	2.478	2.478	2.472
Pt1-N22	2.124	2.111	2.098	2.124	2.133	2.131
Pt1-C3	2.023	2.032	1.984	2.031	2.036	2.032
Pt1-P45	2.300	2.289	2.339	2.306	2.315	2.292
P45-C23	1.838	1.856	1.839	1.847	1.843	1.842
P45-C34	1.832	1.850	1.845	1.845	1.842	1.845
P45-C46	1.871	1.869	1.863	1.866	1.887	1.869
Cl2-Pt1-N22	92.31	91.39	90.95	91.04	89.29	90.52
Cl2-Pt1-P45	91.06	91.29	91.15	92.78	93.52	91.86
N22-Pt1-C3	79.75	80.07	81.39	79.74	80.63	80.71
C3-Pt1-P45	98.07	97.45	96.57	96.96	96.52	97.03
Pt1-N22-C7	114.28	114.73	113.76	114.36	112.73	112.65
Pt1-C3-C4	114.35	113.89	113.06	114.07	112.42	112.46
Pt1-P45-C46	111.02	113.46	113.73	117.25	112.85	118.23
N22-Pt1-P45	170.91	175.37	175.91	174.06	177.03	177.18
Cl2-Pt1-C3	168.25	170.78	172.18	168.49	169.83	169.71
Bond distance or angle	5a (T ₁)	5b (T ₁)	5c (T ₁)	5d (T ₁)	6a (T ₁)	6b (T ₁)
Pt1-Cl2	2.459	2.470	2.470	2.466	2.458	2.453
Pt1-N22	2.098	2.080	2.088	2.098	2.120	2.120
Pt1-C3	1.980	1.991	1.984	1.983	2.018	2.015
Pt1-P45	2.323	2.314	2.330	2.328	2.334	2.309
P45-C23	1.836	1.850	1.840	1.843	1.843	1.842
P45-C34	1.832	1.854	1.847	1.845	1.841	1.845
P45-C46	1.870	1.868	1.864	1.864	1.882	1.869
Cl2-Pt1-N22	92.27	91.17	91.17	91.48	90.23	91.42
Cl2-Pt1-P45	90.24	90.58	90.33	91.37	92.39	90.94
N22-Pt1-C3	80.96	81.40	81.49	80.87	80.24	80.31
C3-Pt1-P45	98.08	97.10	97.16	97.32	97.17	97.51
Pt1-N22-C7	113.55	114.13	113.92	113.58	113.09	112.98
Pt1-C3-C4	112.77	112.68	112.95	112.71	113.41	113.43
Pt1-P45-C46	111.21	113.21	113.21	118.03	112.53	118.57
N22-Pt1-P45	172.64	176.03	176.46	174.68	177.32	177.01
Cl2-Pt1-C3	165.33	171.23	171.97	164.79	169.54	169.77

Table S5. Energies of selected molecular orbitals of the monomer complexes and their compositions in singlet and triplet state (L'=Phosphine ligand).

		Complex 3a					Complex 3b					Complex 3c				
State	MO	Energy (eV)	Components(%)			Energy (eV)	Components(%)			Energy (eV)	Components(%)					
			Pt	L'	ppy		Pt	L'	ppy		Pt	L'	Ppy			
Singlet	LUMO+4	-1.287	6	82	12	-1.710	7	91	2	-1.290	5	92	4			
	LUMO+3	-1.395	4	93	3	-1.938	6	87	7	-1.311	13	72	15			
	LUMO+2	-1.437	2	17	81	-2.132	6	93	2	-1.444	3	16	80			
	LUMO+1	-1.602	19	68	13	-2.215	16	61	22	-1.482	17	70	13			
	LUMO	-2.229	6	15	79	-2.442	7	40	53	-2.211	6	14	80			
	HOMO	-6.471	26	3	71	-6.675	21	3	76	-6.478	25	4	71			
	HOMO-1	-6.864	24	9	67	-7.067	14	4	82	-6.839	15	10	75			
	HOMO-2	-6.920	59	27	14	-7.222	76	11	13	-6.920	72	12	16			
	HOMO-3	-7.136	23	57	20	-7.552	1	97	2	-7.160	12	66	22			
	HOMO-4	-7.395	25	68	7	-7.572	1	96	3	-7.386	21	73	6			
Triplet	HSOMO	-3.497	5	7	88	-3.677	4	9	87	-3.489	5	6	89			
	LSOMO	-7.046	37	16	46	-7.272	40	5	55	-7.009	32	22	46			
		Complex 3d					Complex 4a									
State	MO	Energy (eV)	Components(%)			Energy (eV)	Components(%)									
			Pt	L'	ppy		Pt	L'	bhq							
Singlet	LUMO+4	-1.413	1	49	49	-1.294	6	75	18							
	LUMO+3	-1.466	17	68	15	-1.413	4	93	3							
	LUMO+2	-1.522	2	58	40	-1.547	17	66	18							
	LUMO+1	-1.577	14	80	6	-1.762	9	23	68							
	LUMO	-2.294	7	20	74	-2.346	5	10	85							
	HOMO	-6.479	29	3	68	-6.270	17	5	78							
	HOMO-1	-6.913	27	12	61	-6.824	18	5	77							
	HOMO-2	-6.942	57	12	32	-6.956	59	16	25							
	HOMO-3	-7.167	21	61	18	-7.194	22	50	28							
	HOMO-4	-7.400	19	75	6	-7.406	27	59	14							
Triplet	HSOMO	-3.533	5	8	87	-3.397	3	5	92							
	LSOMO	-7.078	35	13	52	-6.820	27	7	67							

Table S6. Energies of selected molecular orbitals of the dimer complexes and their compositions in singlet and triplet state (L'=Phosphine ligand).

		Complex 5a					Complex 5b					Complex 5c				
State	MO	Energy (eV)	Components(%)				Energy (eV)	Components(%)				Energy (eV)	Components(%)			
			Pt	L'	ppy	Cl		Pt	L'	ppy	Cl		Pt	L'	Ppy	Cl
Singlet	LUMO+4	-0.938	10	81	7	2	-1.505	16	72	10	2	-1.024	1	4	95	0
	LUMO+3	-1.030	2	5	94	0	-1.580	16	76	8	1	-1.077	23	66	11	1
	LUMO+2	-1.081	27	52	20	2	-1.668	24	65	10	2	-1.106	31	52	14	3
	LUMO+1	-1.182	26	62	11	2	-1.851	5	10	84	1	-1.728	5	5	89	1
	LUMO	-1.762	6	5	88	1	-1.875	7	15	78	1	-1.753	5	5	89	1
	HOMO	-5.802	46	1	37	16	-5.950	43	1	42	14	-5.776	46	1	38	15
	HOMO-1	-5.830	46	0	41	13	-6.493	77	5	15	3	-5.820	46	0	40	13
	HOMO-2	-6.305	80	10	9	2	-6.507	81	5	11	2	-6.302	83	8	7	2
	HOMO-3	-6.357	85	9	6	0	-6.570	27	3	68	3	-6.344	85	9	5	1
	HOMO-4	-6.481	10	2	83	5	-6.594	21	2	72	5	-6.466	14	2	78	6
Triplet	HSOMO	-2.948	5	3	92	1	-3.055	5	4	91	1	-2.385	6	4	89	1
	LSOMO	-5.812	46	1	37	16	-5.949	44	1	41	15	-6.164	35	0	53	12
		Complex 5d					Complex 6a					Complex 6b				
State	MO	Energy (eV)	Components(%)				Energy (eV)	Components(%)				Energy (eV)	Components(%)			
			Pt	L'	ppy	Cl		Pt	L'	bhq	Cl		Pt	L'	Bhq	Cl
Singlet	LUMO+4	-1.037	7	16	76	1	-1.233	10	71	17	2	-1.110	27	53	16	4
	LUMO+3	-1.076	26	47	22	4	-1.323	7	11	81	1	-1.290	5	6	88	1
	LUMO+2	-1.209	27	57	14	2	-1.349	8	37	53	2	-1.312	7	7	84	1
	LUMO+1	-1.747	6	6	87	1	-1.872	3	12	84	0	-1.851	3	5	92	0
	LUMO	-1.775	6	7	87	1	-1.907	3	5	92	0	-1.895	3	6	91	0
	HOMO	-5.788	46	1	37	16	-5.705	36	2	49	13	-5.685	37	1	50	12
	HOMO-1	-5.859	46	1	42	12	-5.766	34	1	56	9	-5.719	35	2	54	9
	HOMO-2	-6.230	78	11	8	2	-6.308	77	12	8	3	-6.320	85	9	5	1
	HOMO-3	-6.322	79	13	6	2	-6.399	82	8	9	1	-6.386	77	7	12	5
	HOMO-4	-6.483	16	3	75	5	-6.439	25	7	64	4	-6.425	20	3	72	5
Triplet	HSOMO	-2.914	6	4	90	1	-2.828	3	4	94	0	-2.812	2	3	95	0
	LSOMO	-5.870	46	1	42	12	-5.781	34	1	56	9	-5.731	35	1	55	9

Table S7. Plots of HOMO and LUMO orbitals for the singlet and LSOMO and HSOMO for the triplet states of the monomer complexes.

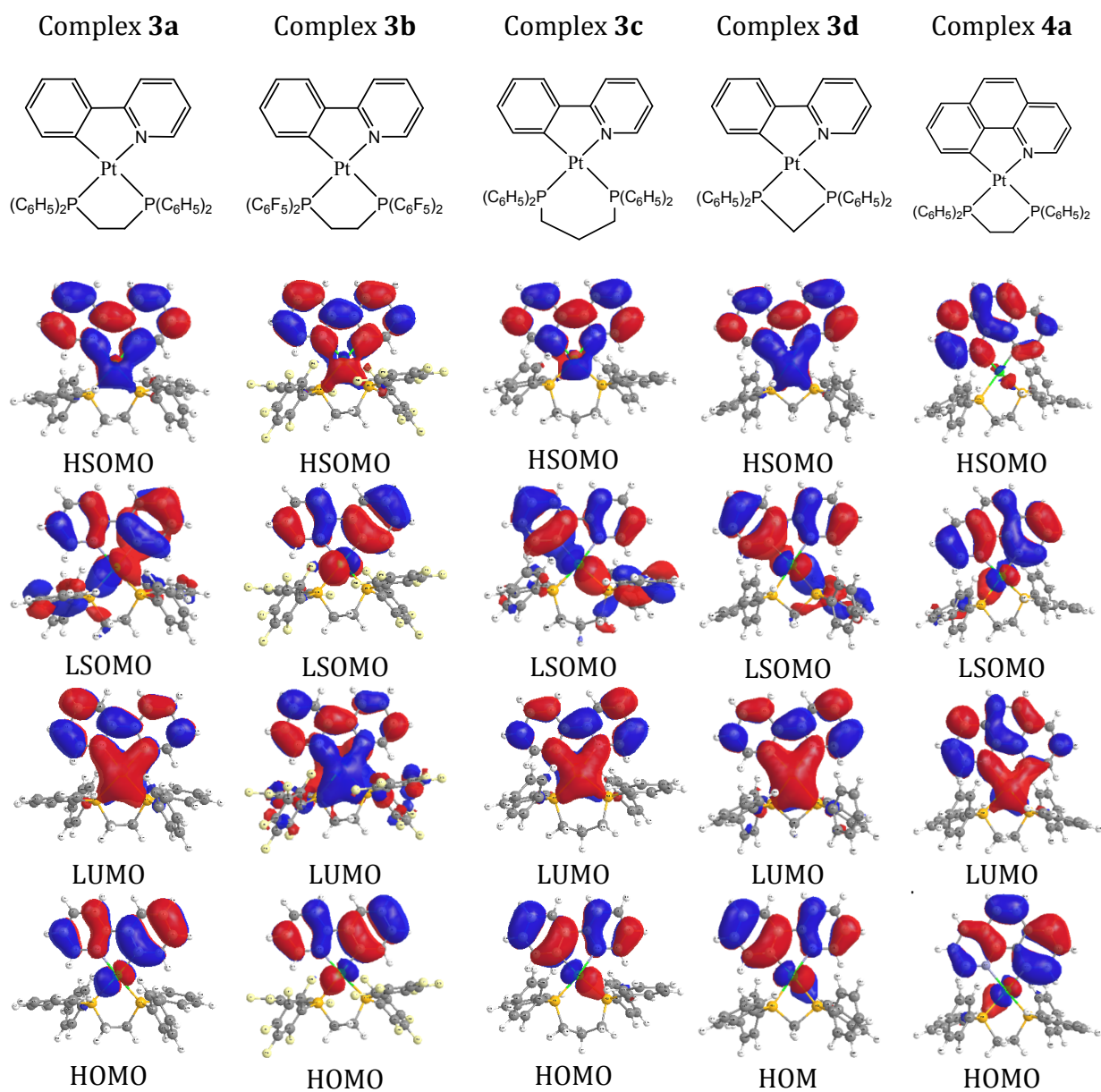
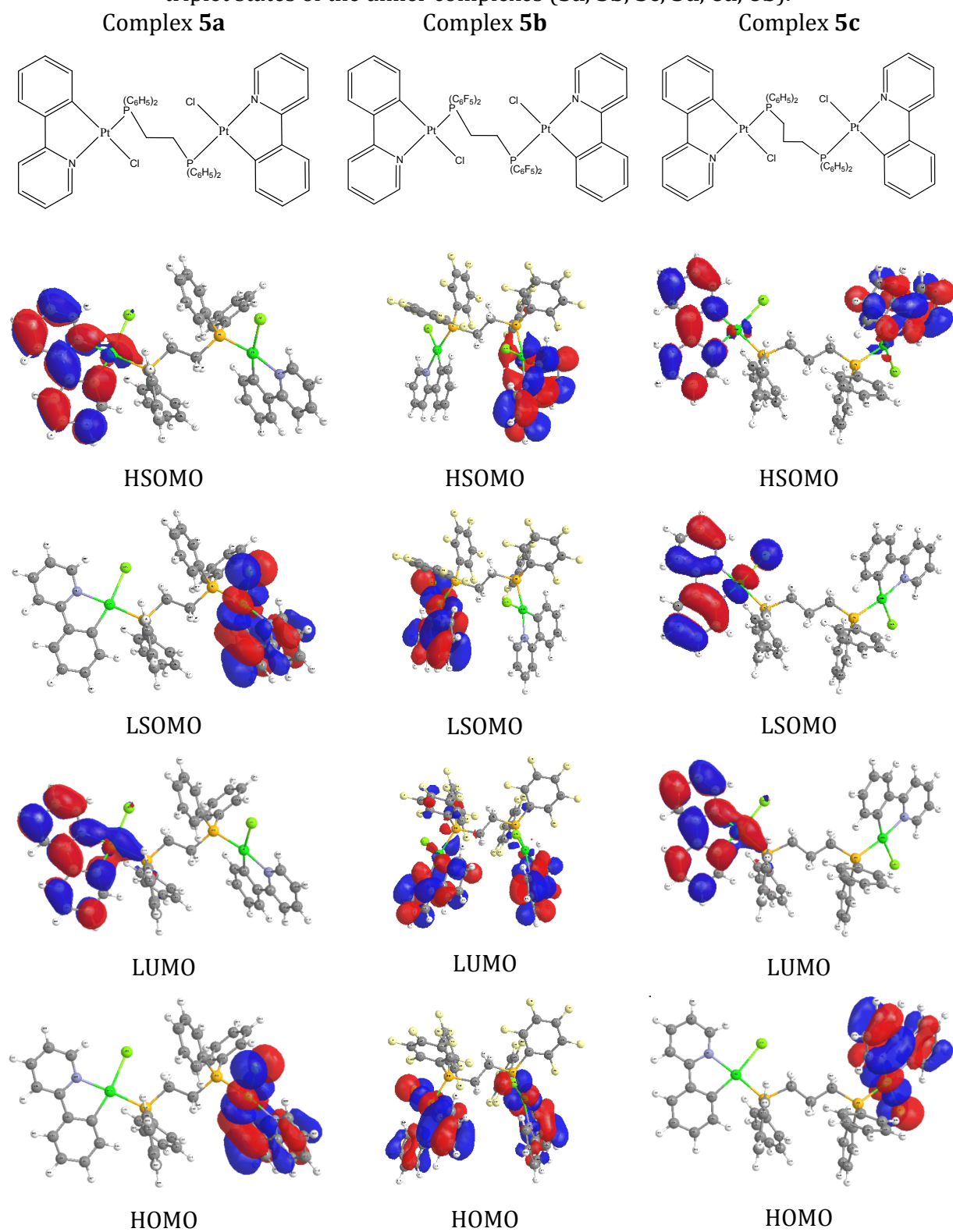
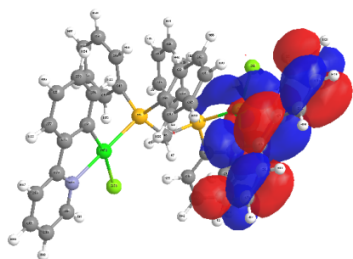
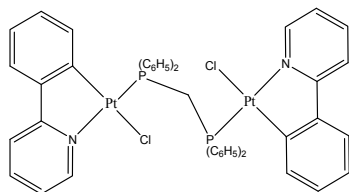


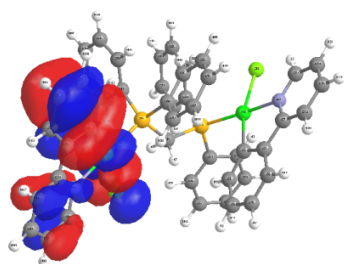
Table S8. Plots of HOMO and LUMO orbitals for the singlet and HSOMO and LSOMO of triplet states of the dimer complexes (**5a**, **5b**, **5c**, **5d**, **6a**, **6b**).



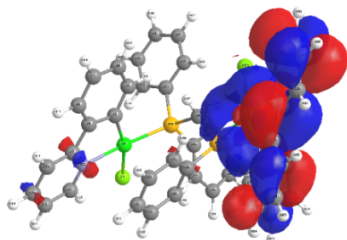
Complex 5d



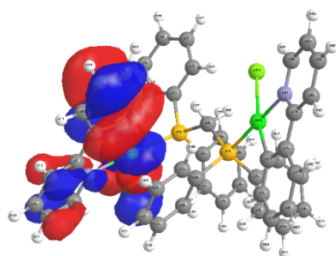
HSOMO



LSOMO

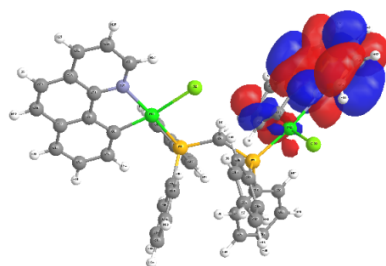
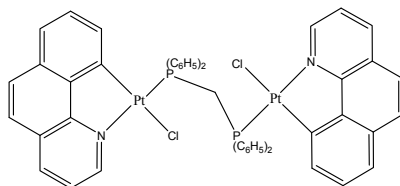


LUMO

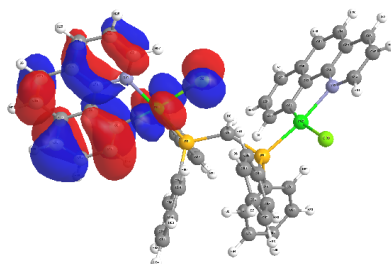


HOMO

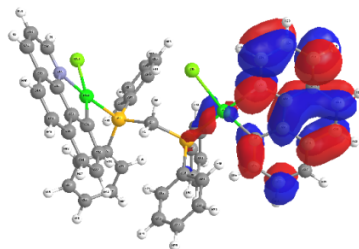
Complex 6a



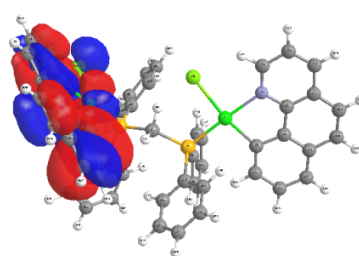
HSOMO



LSOMO

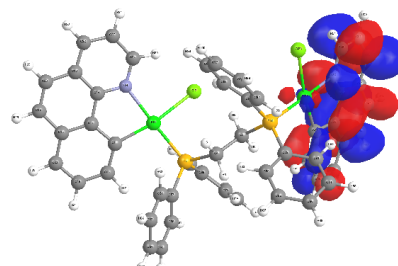
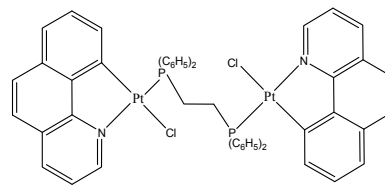


LUMO

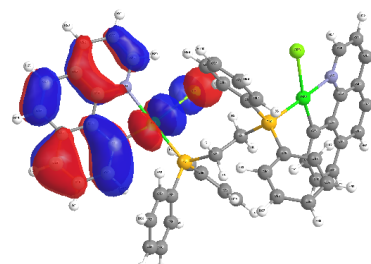


HOMO

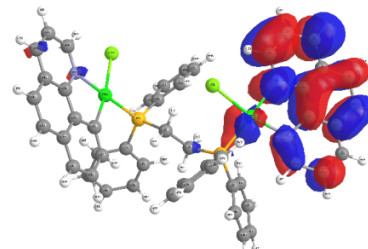
Complex 6b



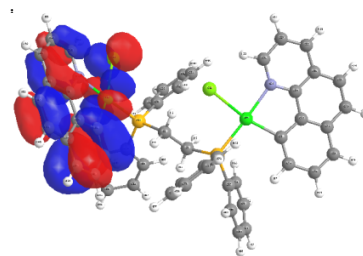
HSOMO



LSOMO



LUMO



HOMO