Dalton Transactions

Supporting Information

Platinum Complexes Bearing Normal and Mesoionic N-Heterocyclic Carbene Based Pincer Ligands: Syntheses, Structures, and Photo-Functional Attributes

Abbas Raja Naziruddin, Chen-Shiang Lee, Wan-Jung Lin, Bing-Jian Sun, Kang-Heng Chao, Agnes Hsiu Hwa Chang*, and Wen-Shu Hwang*

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Corresponding Author Address: Department of Chemistry, National Dong Hwa University, Hualien 974, Taiwan, ROC. Fax: +886 3 8632000; Tel: +886 3 8632001; Corresponding Authors*
E-mail: hws@mail.ndhu.edu.tw.

Figure S1: Molecular Structure of **1**·PF_6.

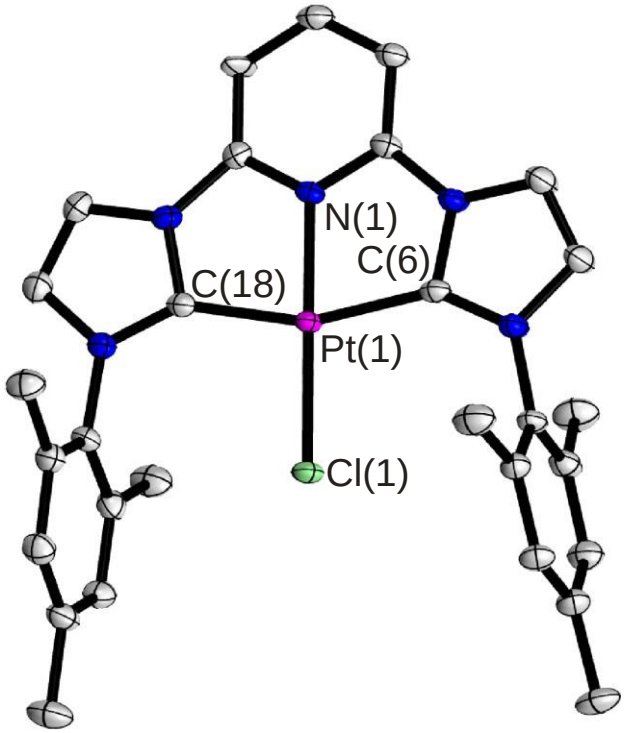


Figure S2: (**a.**) Emission spectra of **2** and **3** in acetonitrile solution.

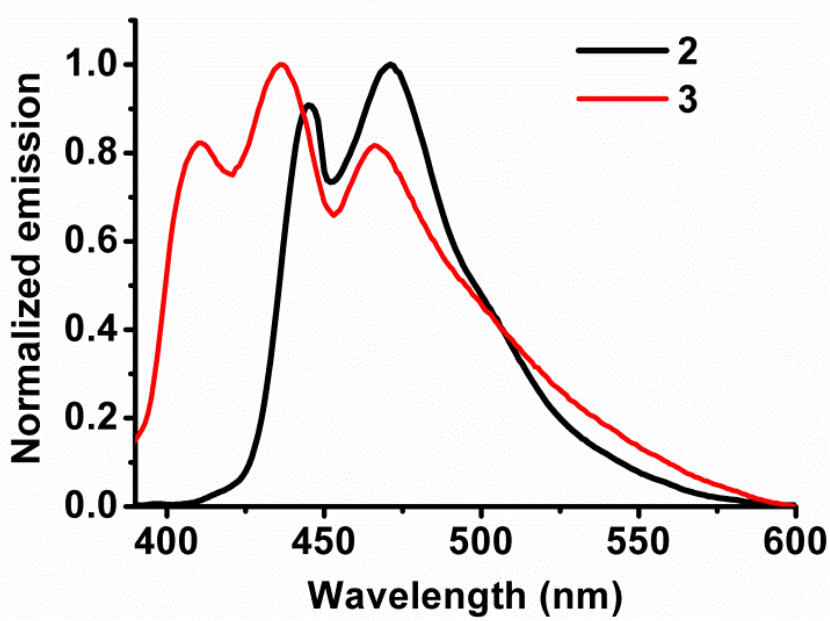


Figure S2: (**b**.) Emission spectra of **4**, **5**, and **6** in acetonitrile solution.

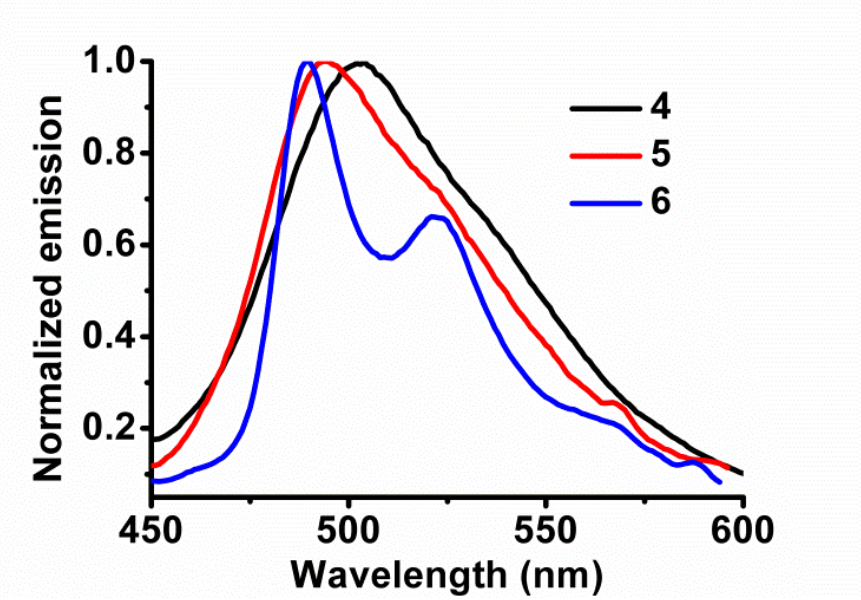


Table S1. Crystal data and structure refinement for Pt complexes

Complex	**1**	**2**	**3**	**2·H_2O**
Empirical formula	$C_{32}H_{35}ClF_6N_5OPPt$	$C_{33}H_{35}F_{12}N_7P_2Pt$	$C_{31}H_{31}Cl_2F_6N_6PPt$	$C_{31}H_{34}F_{12}N_6OP_2Pt$
Formula weight	881.16	1014.71	898.58	991.67
Temperature (K)	100(2)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	monoclinic	Monoclinic	Monoclinic
space group	P2(1)/c	P2(1)/c	Cc	P2(1)/c
a (Å)	10.3785(8)	23.1671(10)	19.7610(5)	19.3773(19)
b (Å)	20.6873(17)	8.6136(3)	13.1217(3)	8.4921(9)
c (Å)	15.9606(13)	20.8355(9)	15.7217(6)	22.294(2)
α (°)	90.00	90.00	90.00	90.00
β (°)	100.8570(10)	113.4630(10)	122.84	92.745(2)
γ (°)	90.00	90.00	90.00	90.00
V ($Å^3$)	3365.5(5)	3813.99	3425.11(18)	3664.4(6)
Z	4	4	4	4
Calculated density ($Mg·m^{-3}$)	1.739	1.767	1.743	1.798
Absorption coefficient (mm^{-1})	4.364	3.857	4.364	4.013
F(000)	1736	1992	1760	1944
h, k, l_{max}	13, 27, 21	28, 10, 25	23, 15, 18	-23<=h<=23, -9<=k<=10, -27<=l<=27
Theta range for data collection (°)	1.63–28.52	0.96–25.50	1.98–25.07	1.83–25.50
Reflections collected / unique	8511/ 7401	7101/ 5769	6028/ 5695	18080/6741
Completeness (%)	99.6	100.0	99.8	98.8
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2

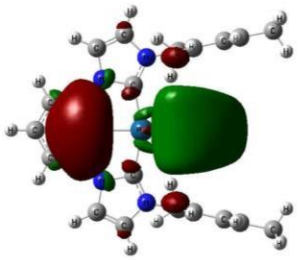
Data / restraints / parameters	8511/0/432	7101/0/504	6028/2/447	6741/0/ 479
Goodness-of-fit on F^2	1.038	1.038	1.042	1.299
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0281 wR_2 = 0.0653	R_1 = 0.0325 wR_2 = 0.0883	R_1 = 0.0306 wR_2 = 0.0807	R_1 = 0.0993 wR_2 = 0.2048
R indices (all data)	R = 0.348 wR_2 = 0.0689	R = 0.0453 wR_2 = 0.1005	R = 0.0333 wR_2 = 0.0822	R_1 = 0.1228 wR_2 = 0.2148
Largest diff. peak and hole(e·Å^{-3})	2.752 and –1.429	0.885 and –0.734	0.777 and –0.315	2.918 and –5.075

Complex	**4**
Empirical formula	C_{29} H_{31} Cl F_6 N_7 P Pt
Formula weight	853.12
Temperature (K)	296(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic,
space group	P2(1)/n
a (Å)	9.1269(5)
b (Å)	25.3776(16)
c (Å)	15.1848(9)
α (°)	90.00
β (°)	106.5720º(10)
γ (°)	90.00
V (Å^3)	3371.0(3) Å^3
Z	4
Calculated density (Mg·m^{-3})	1.681
Absorption coefficient (mm^{-1})	4.353
F(000)	1672
h, k, l_{max}	10, 30, 15
Theta range for data collection (°)	1.60–25.11
Reflections collected / unique	20481 / 5959 [R(int) = 0.0617]
Completeness (%)	99.2
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5959 / 0 / 414
Goodness-of-fit on F^2	0.877
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0447, wR_2 = 0.1182
R indices (all data)	R_1 = 0.0813, wR_2 = 0.1410
Largest diff. peak and hole(e·Å^{-3})	0.760 and –0.501

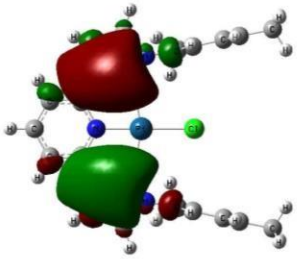
Table S2.1: Orbital diagram of HOMO–14 to LUMO+14 levels of **1** for the singlet states.

S_0 state, B3LYP/SDD

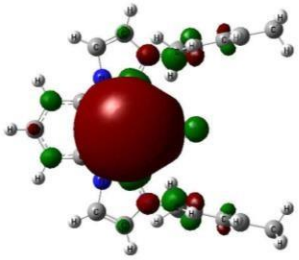
LUMO+14(151) -0.04593



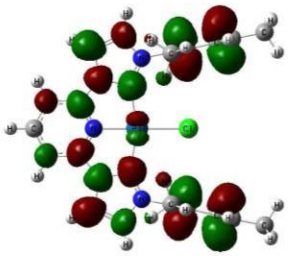
LUMO+13(150) -0.04787



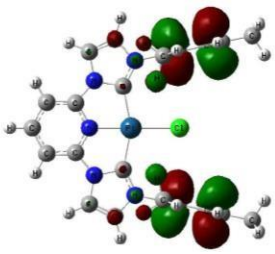
LUMO+12(149) -0.05629



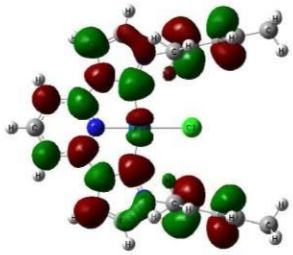
LUMO+11(148) -0.08090



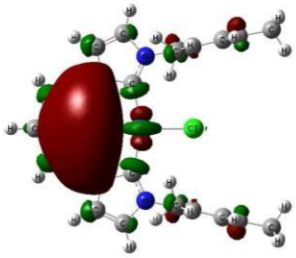
LUMO+10(147) -0.08436



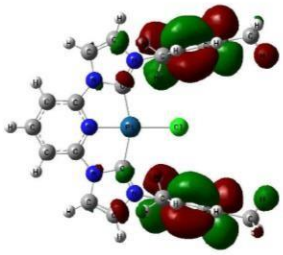
LUMO+9(146) -0.08678



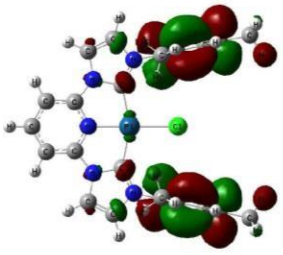
LUMO+8(145) -0.09196



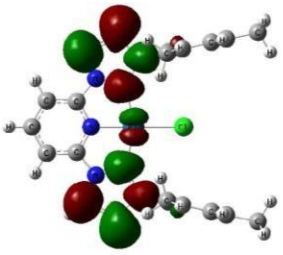
LUMO+7(144) -0.09349



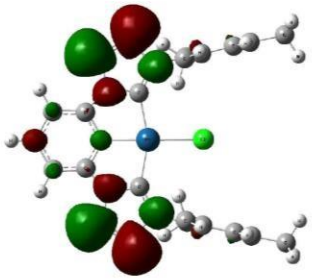
LUMO+6(143) -0.09391



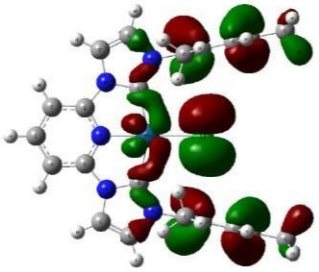
LUMO+5(142) -0.10191



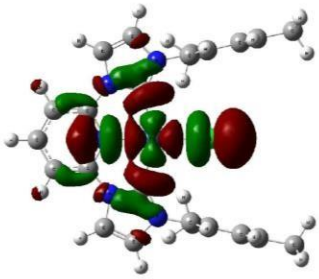
LUMO+4(141) -0.11013



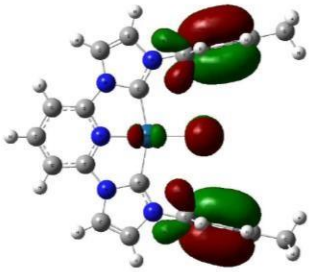
HOMO(136) -0.31729



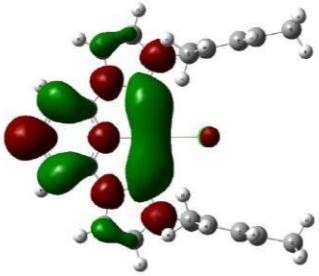
LUMO+3(140) -0.13060



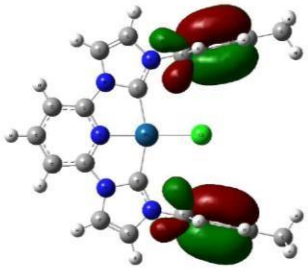
HOMO-1(135) -0.32164



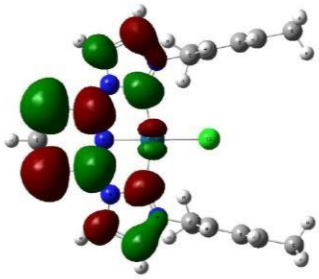
LUMO+2(139) -0.13993



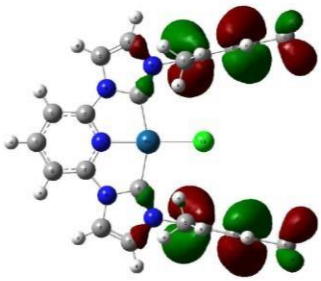
HOMO-2(134) -0.32222



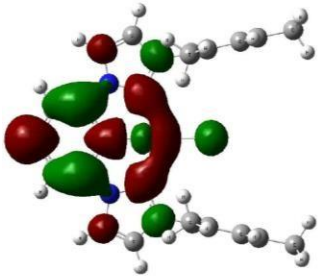
LUMO+1(138) -0.17821



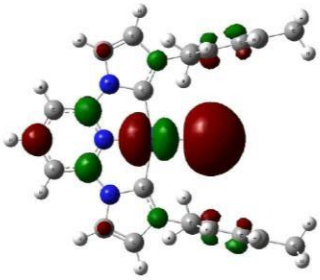
HOMO-3(133) -0.32516



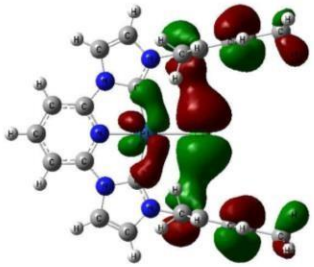
LUMO(137) -0.20428



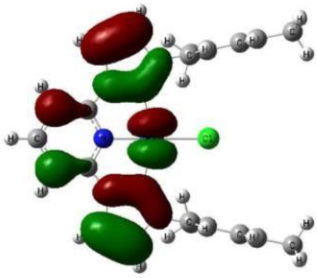
HOMO-4(132) -0.33115



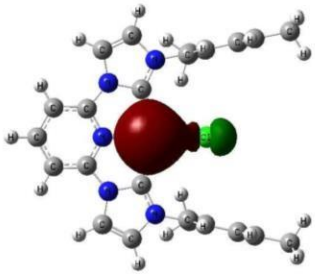
HOMO-5(131) -0.33392



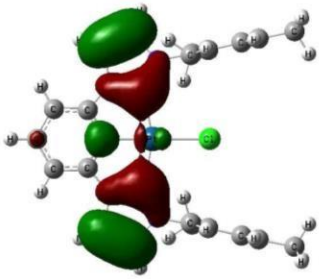
HOMO-6(130) -0.34865



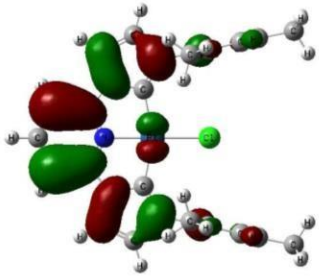
HOMO-7(129) -0.35932



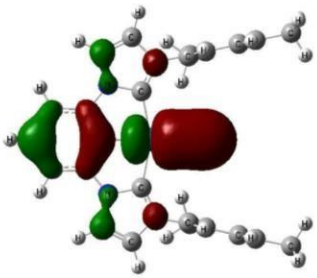
HOMO-8(128) -0.38282



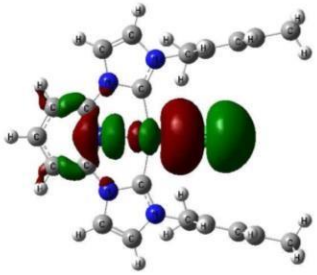
HOMO-9(127) -0.39089



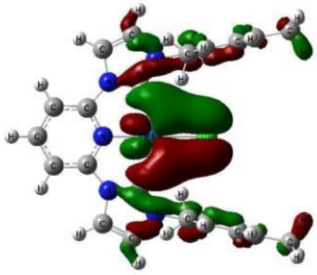
HOMO-10(126) -0.39563



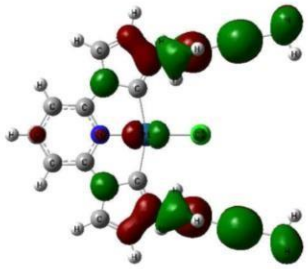
HOMO-11(125) -0.40785



HOMO-12(124) -0.41437



HOMO-13(123) -0.41740



HOMO-14(122) -0.41845

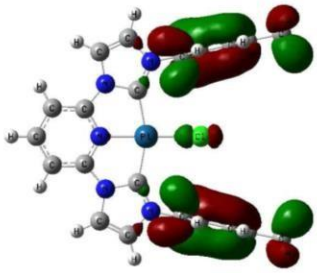
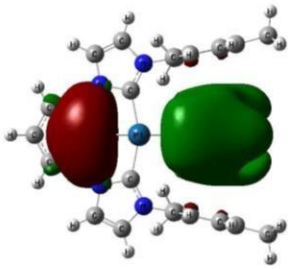


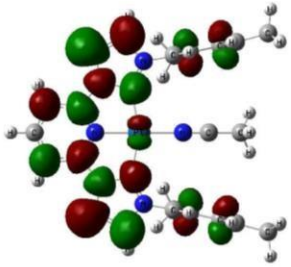
Table S2.2: Orbital diagram of HOMO−14 to LUMO+14 levels of **2** for the singlet states.

S_0 state, B3LYP/SDD

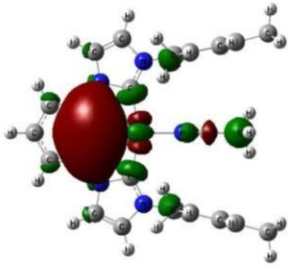
LUMO+14(153) -0.16636



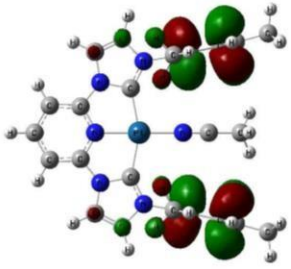
LUMO+13(152) -0.18185



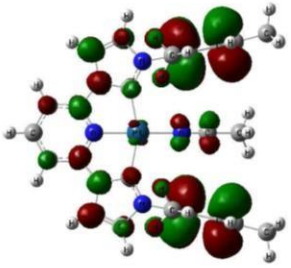
LUMO+12(151) -0.18230



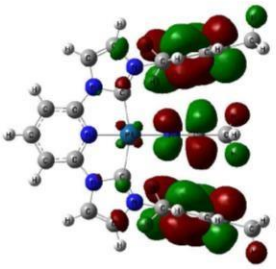
LUMO+11(150) -0.18839



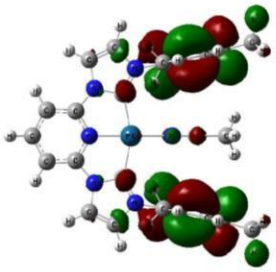
LUMO+10(149) -0.18920



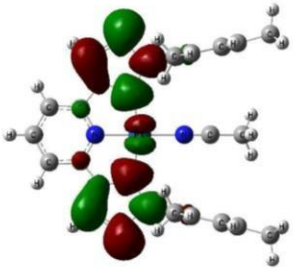
LUMO+9(148) -0.19401



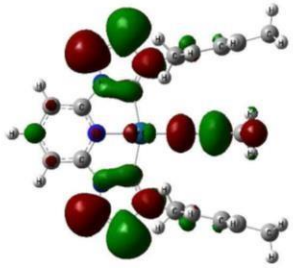
LUMO+8(147) -0.19867



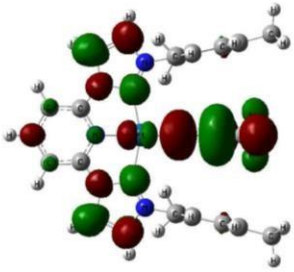
LUMO+7(146) -0.20245



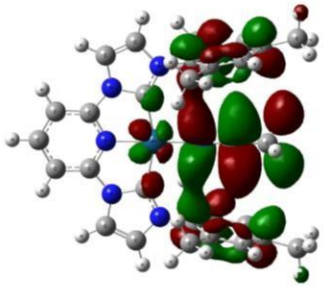
LUMO+6(145) -0.20330



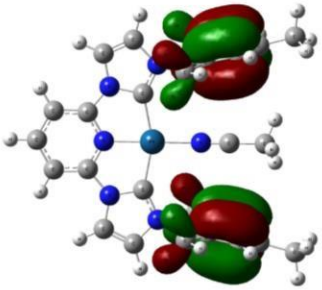
LUMO+5(144) -0.20885



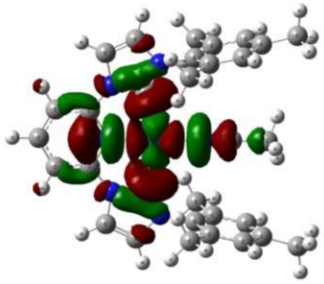
LUMO+4(143) -0.21184



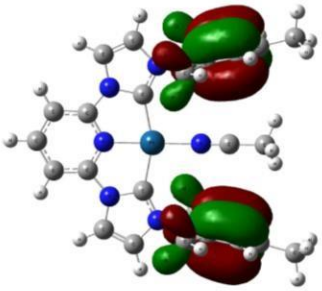
HOMO(138) -0.42650



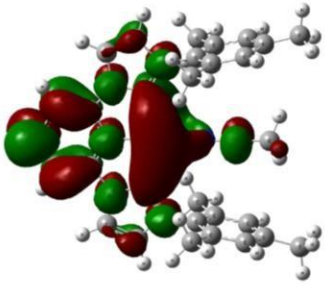
LUMO+3(142) -0.23678



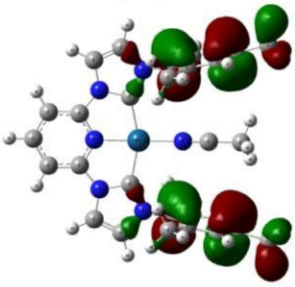
HOMO-1(137) -0.42662



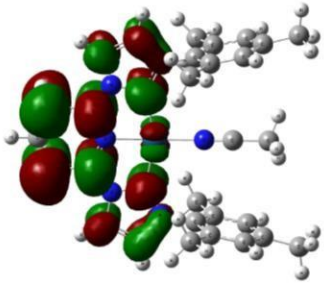
LUMO+2(141) -0.24321



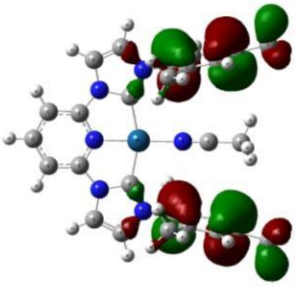
HOMO-2(136) -0.42807



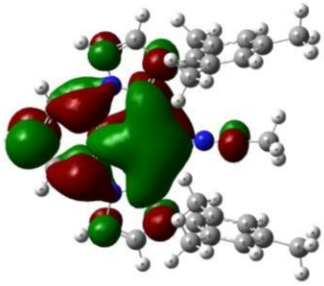
LUMO+1(140) -0.27529



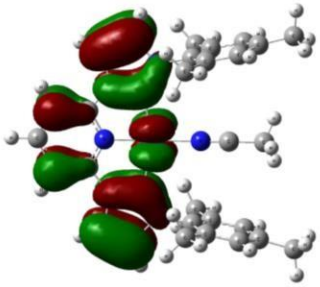
HOMO-3(135) -0.42888



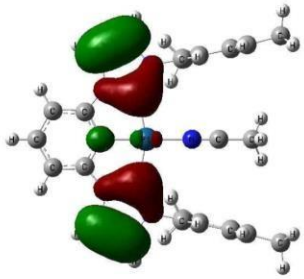
LUMO(139) -0.31124



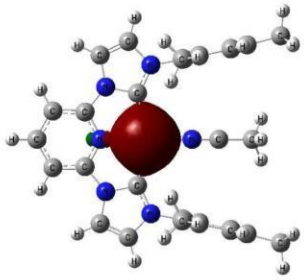
HOMO-4(134) -0.45399



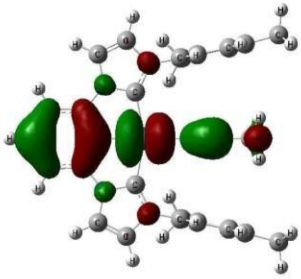
HOMO-5(133) -0.48140



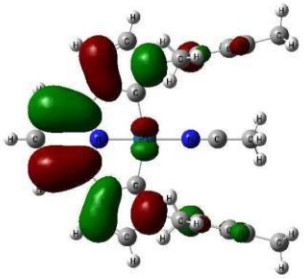
HOMO-6(132) -0.48242



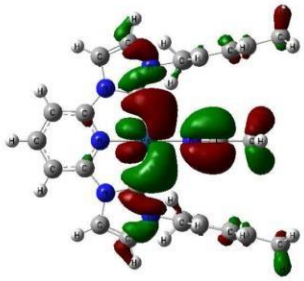
HOMO-7(131) -0.48782



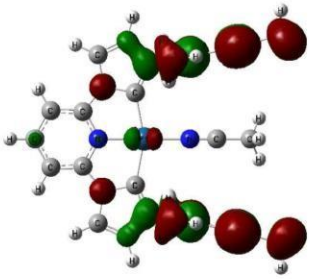
HOMO-8(130) -0.49027



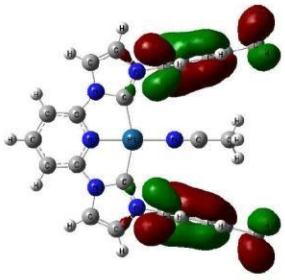
HOMO-9(129) -0.50092



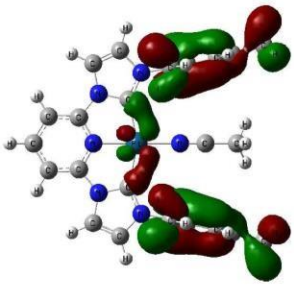
HOMO-10(128) -0.51704



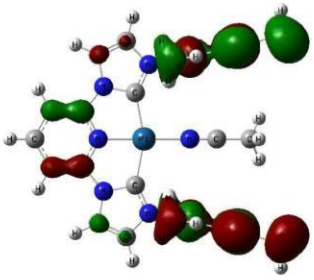
HOMO-11(127) -0.51980



HOMO-12(126) -0.52045



HOMO-13(125) -0.52059



HOMO-14(124) -0.52397

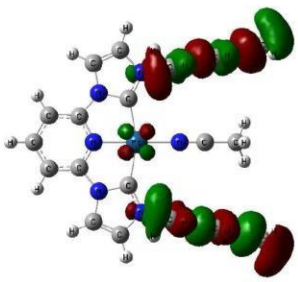
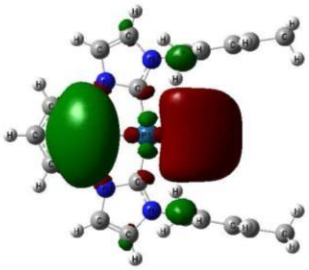


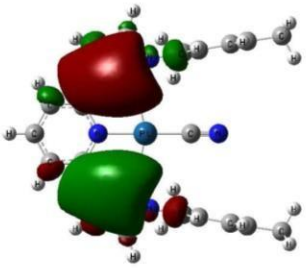
Table S2.3: Orbital diagram of HOMO−14 to LUMO+14 levels of **3** for the singlet states.

S_0 state, B3LYP/SDD

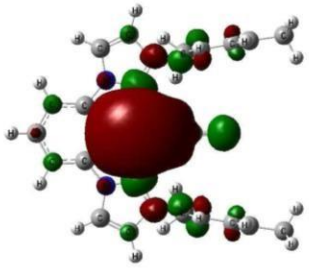
LUMO+14(149) -0.03894



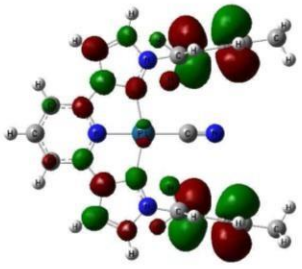
LUMO+13(148) -0.05061



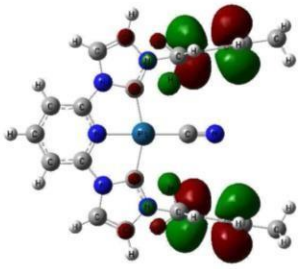
LUMO+12(147) -0.06406



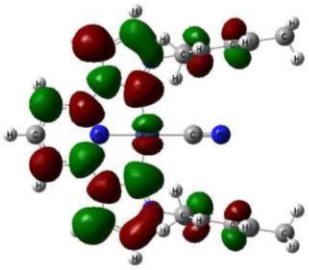
LUMO+11(146) -0.08185



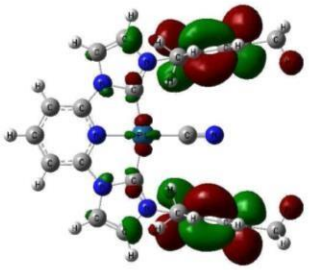
LUMO+10(145) -0.08429



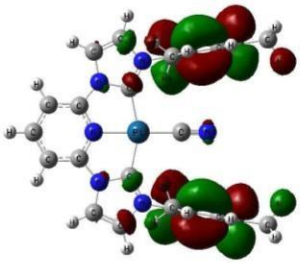
LUMO+9(144) -0.08940



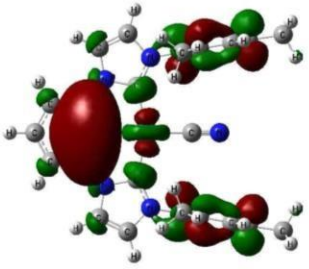
LUMO+8(143) -0.09374



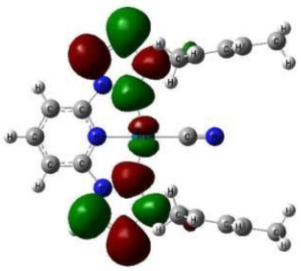
LUMO+7(142) -0.09417



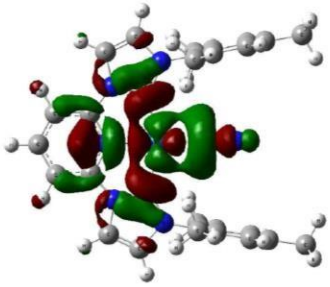
LUMO+6(141) -0.09472



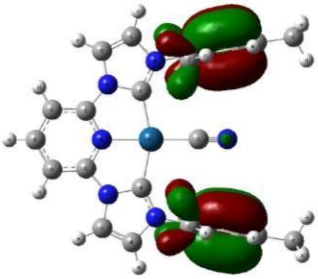
LUMO+5(140) -0.10504



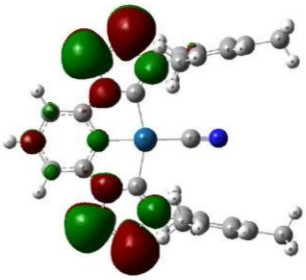
LUMO+4(139) -0.10657



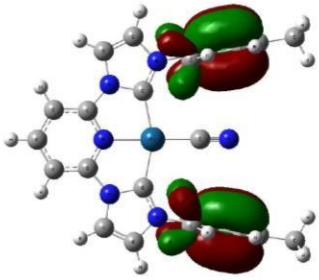
HOMO(134) -0.32195



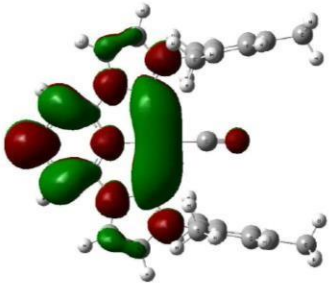
LUMO+3(138) -0.11302



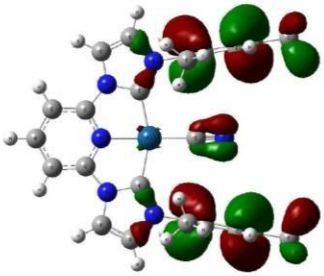
HOMO-1(133) -0.32217



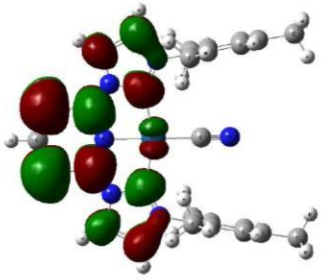
LUMO+2(137) -0.14511



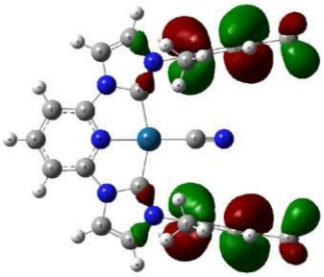
HOMO-2(132) -0.32413



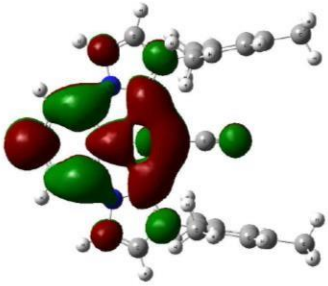
LUMO+1(136) -0.18175



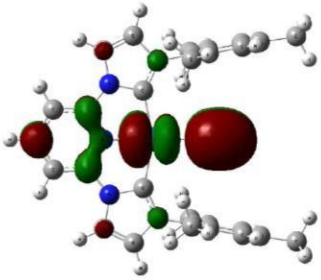
HOMO-3(131) -0.32476



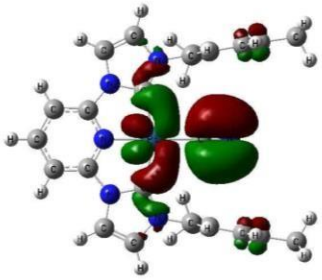
LUMO(135) -0.20975



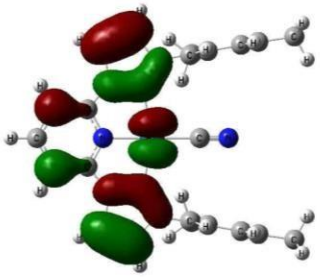
HOMO-4(130) -0.35154



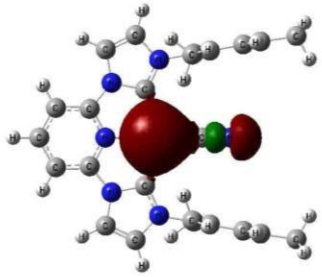
HOMO-5(129) -0.35187



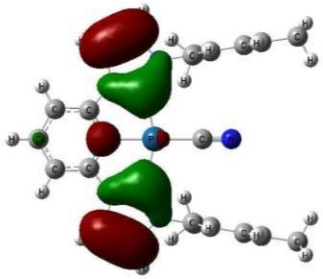
HOMO-6(128) -0.35248



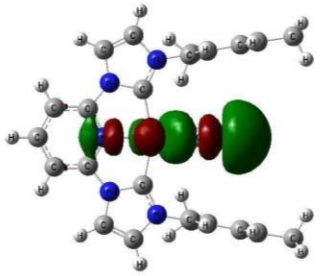
HOMO-7(127) -0.36269



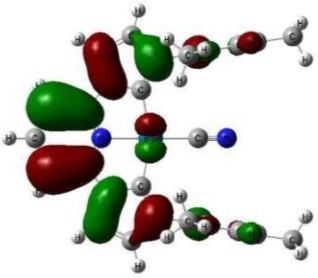
HOMO-8(126) -0.38607



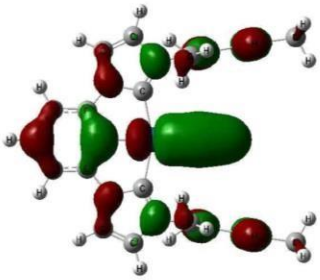
HOMO-9(125) -0.38977



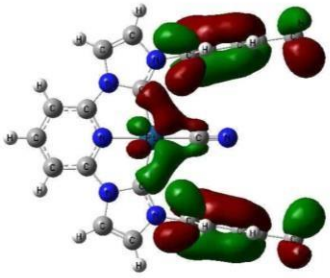
HOMO-10(124) -0.39424



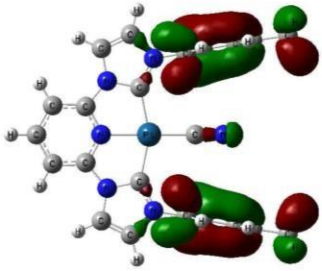
HOMO-11(123) -0.41226



HOMO-12(122) -0.41847



HOMO-13(121) -0.41876



HOMO-14(120) -0.41935

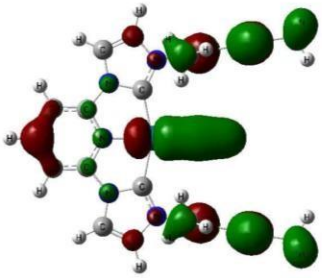
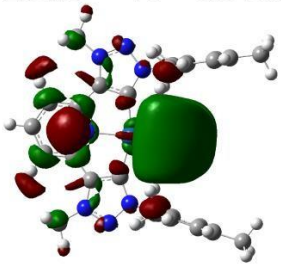


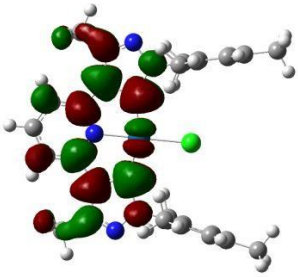
Table S2.4: Orbital diagram of HOMO−14 to LUMO+14 levels of **4** for the singlet states.

S_0 state, B3LYP/SDD

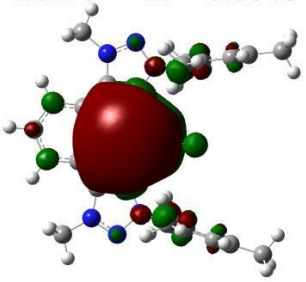
LUMO + 14 -0.04064



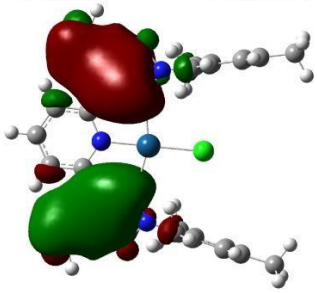
LUMO + 13 -0.04646



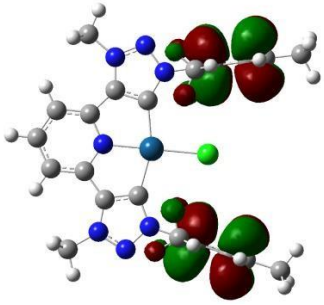
LUMO + 12 -0.05181



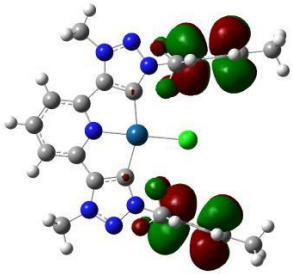
LUMO + 11 -0.05934



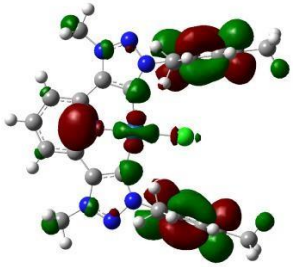
LUMO + 10 -0.07929



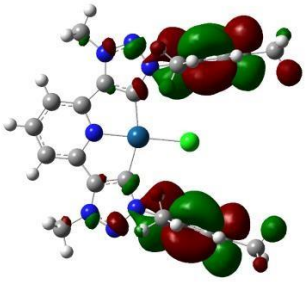
LUMO + 9 -0.08030



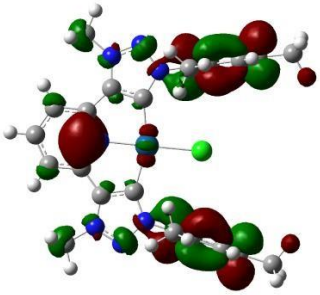
LUMO + 8 -0.09018



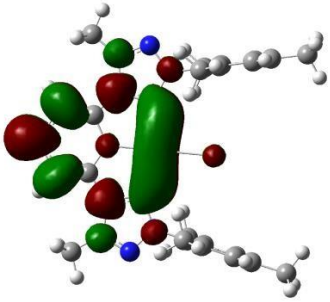
LUMO + 7 -0.09292



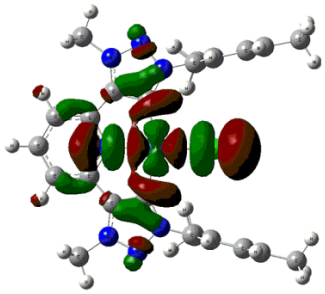
LUMO + 6 -0.09570



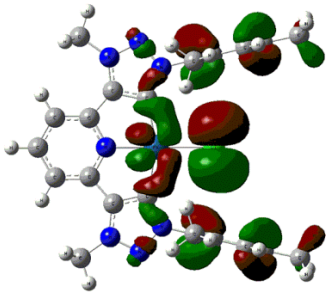
LUMO + 5 0.10708



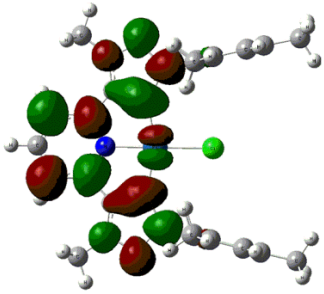
LUMO+4 -0.12044



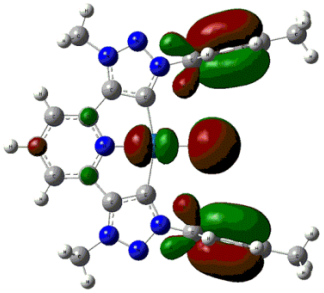
HOMO -0.31193



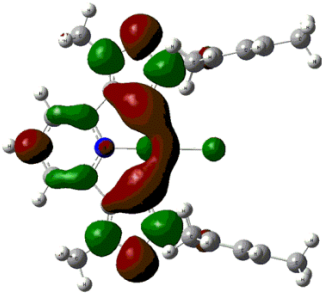
LUMO+3 -0.13588



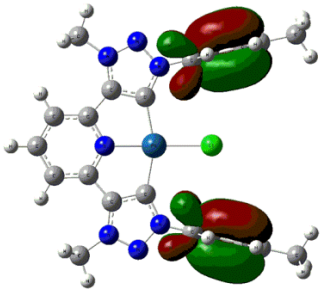
HOMO-1 -0.31766



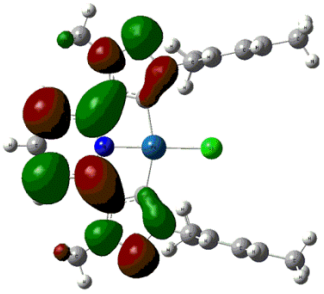
LUMO+2 -0.16910



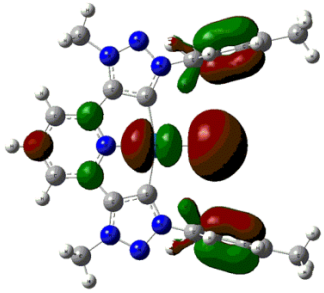
HOMO-2 -0.31881



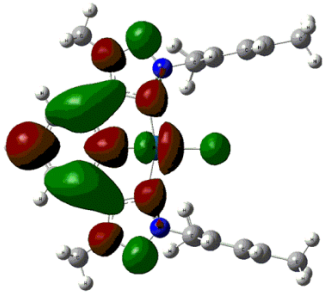
LUMO+1 -0.19814



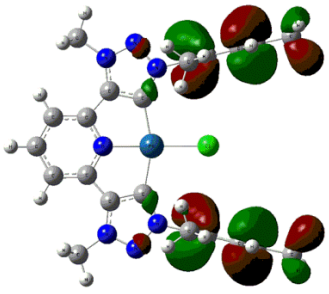
HOMO-3 -0.32200



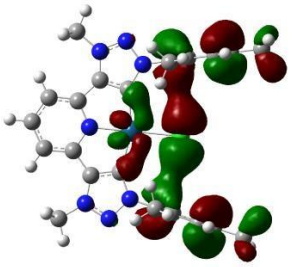
LUMO -0.20543



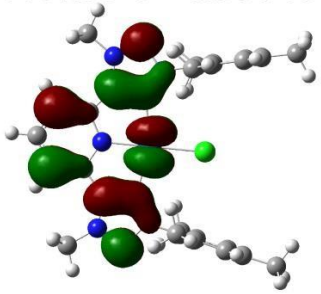
HOMO-4 -0.32270



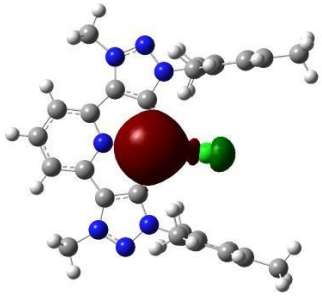
HOMO-5 0.32719



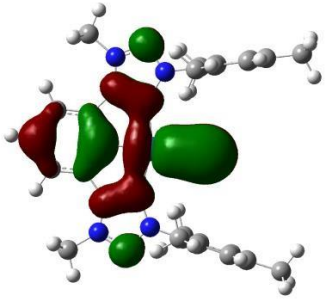
HOMO-6 0.33813



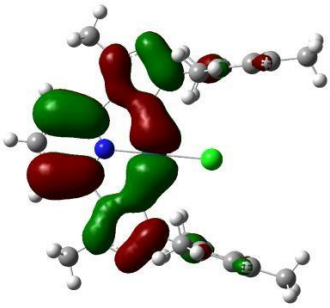
HOMO-7 0.34436



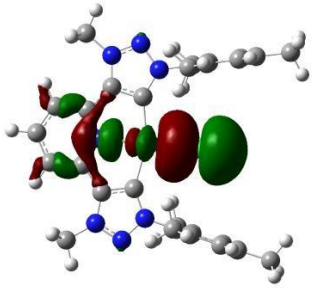
HOMO-8 -0.38171



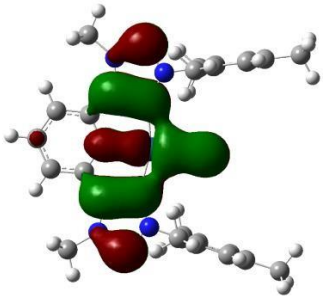
HOMO-9 -0.39459



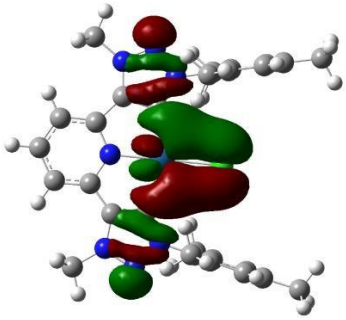
HOMO-10 0.39721



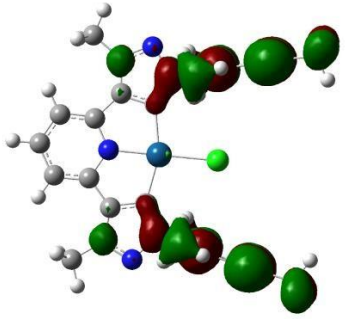
HOMO-11 0.39858



HOMO-12 -0.39952



HOMO-13 -0.41439



HOMO-14 -0.41530

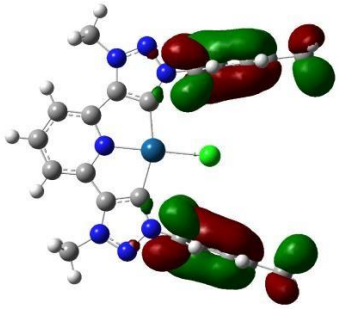
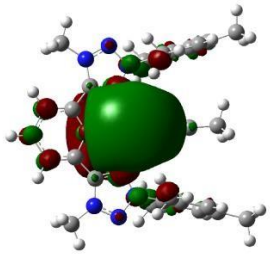


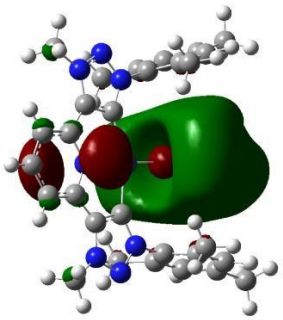
Table S2.5: Orbital diagram of HOMO−14 to LUMO+14 levels of **5** for the singlet states.

S0 state, B3LYP/SDD

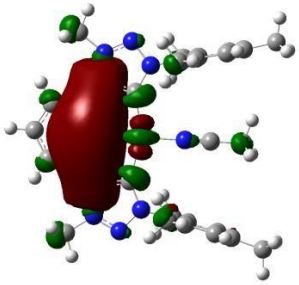
LUMO + 14 -0.15112



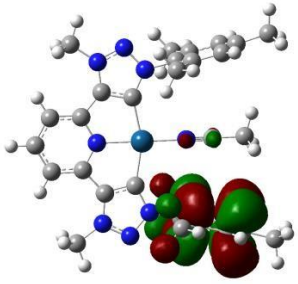
LUMO + 13 -0.16273



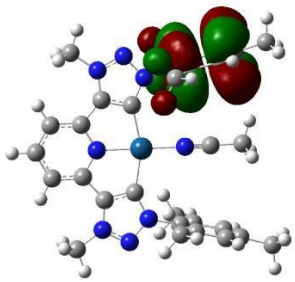
LUMO + 12 -0.18049



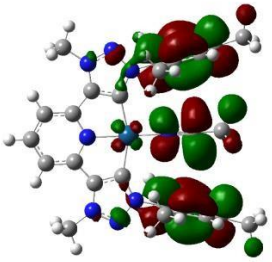
LUMO + 11 -0.18111



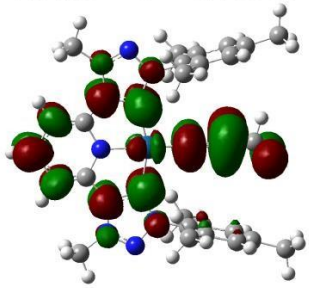
LUMO + 10 -0.18265



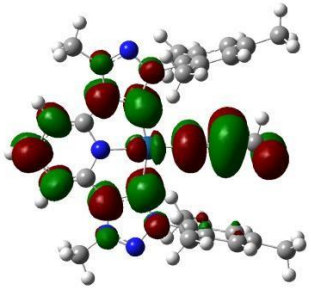
LUMO + 9 -0.19023



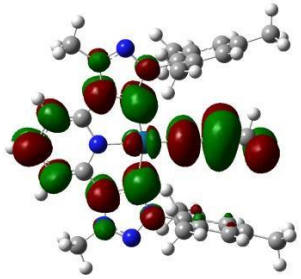
LUMO + 8 -0.19304



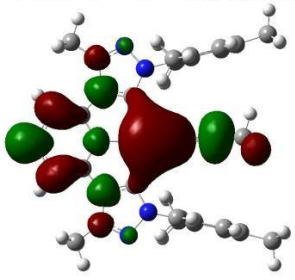
LUMO + 7 -0.19478



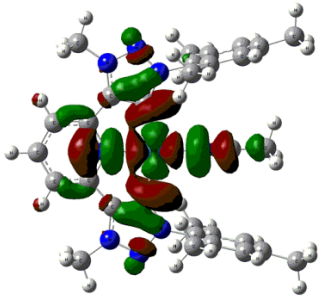
LUMO + 6 -0.20412



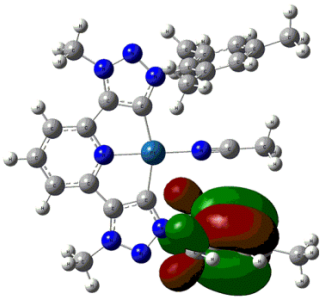
LUMO + 5 -0.21389



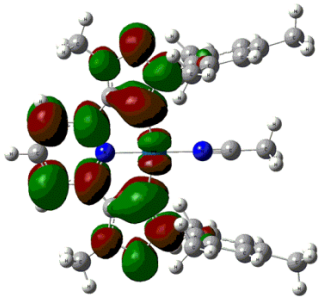
LUMO+4 -0.22487



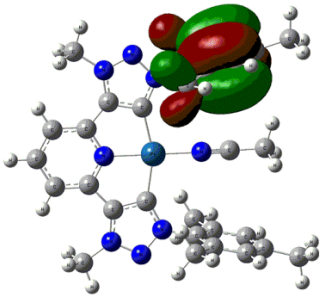
HOMO -0.41992



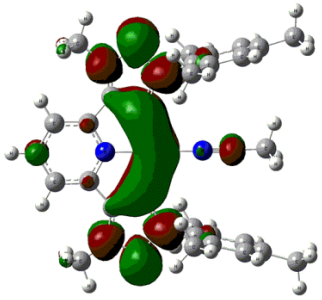
LUMO+3 -0.23631



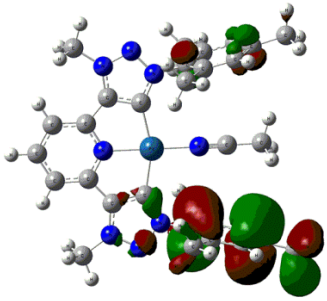
HOMO-1 -0.42111



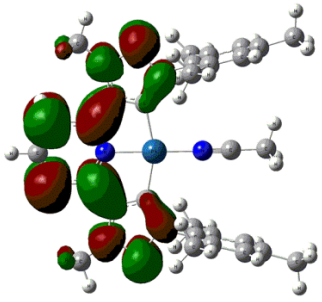
LUMO+2 -0.27020



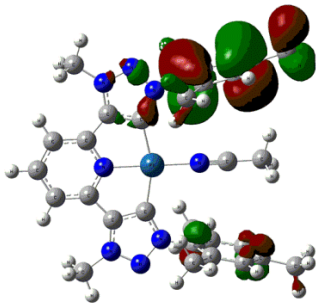
HOMO-2 -0.42277



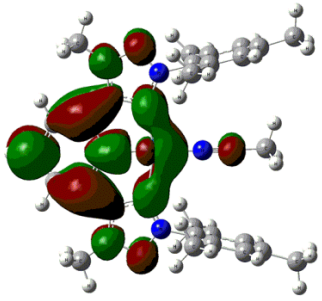
LUMO+1 -0.29243



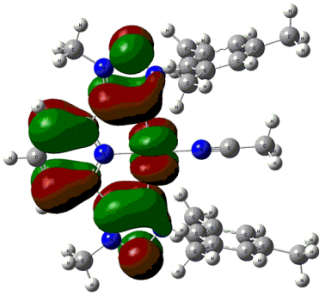
HOMO-3 -0.42426



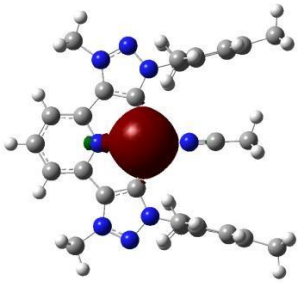
LUMO -0.30774



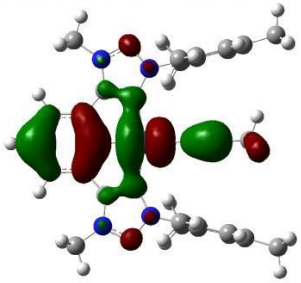
HOMO-4 -0.44535



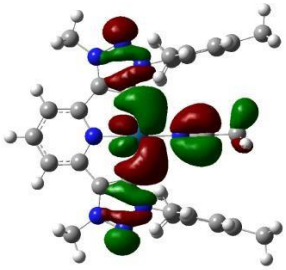
HOMO-5 -0.46632



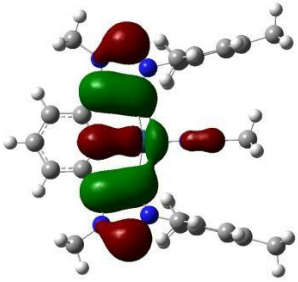
HOMO-6 -0.47487



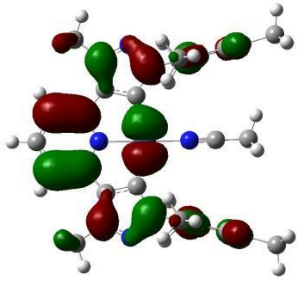
HOMO-7 -0.48582



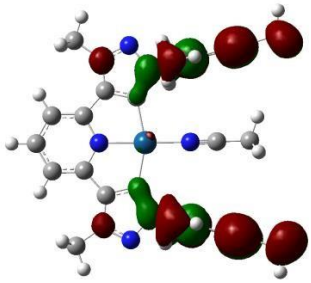
HOMO-8 -0.449753



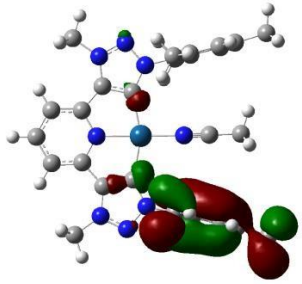
HOMO-9 -0.49922



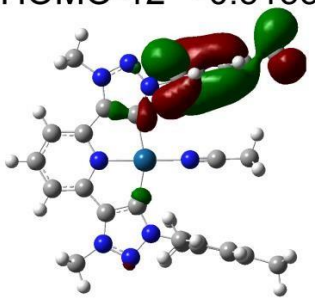
HOMO-10 -0.51173



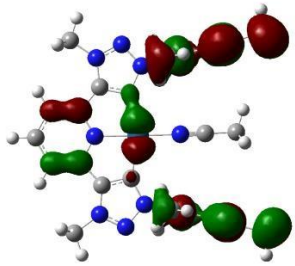
HOMO-11 -0.51355



HOMO-12 -0.51558



HOMO-13 -0.51546



HOMO-14 -0.51787

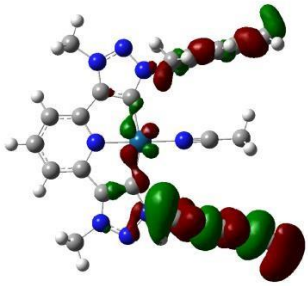
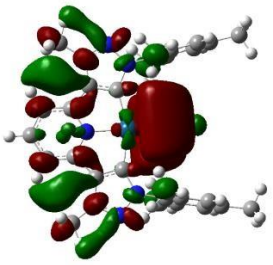


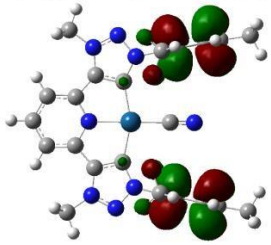
Table S2.6: Orbital diagram of HOMO−14 to LUMO+14 levels of **6** for the singlet states.

S0 state, B3LYP/SDD

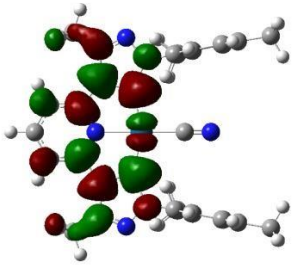
LUMO + 14 0.03728



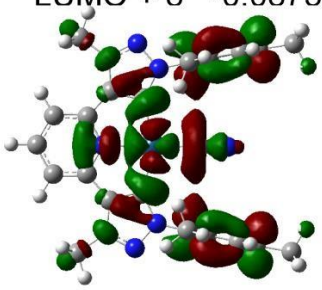
LUMO + 9 -0.08018



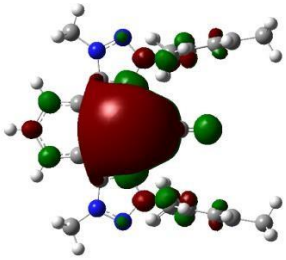
LUMO + 13 -0.05077



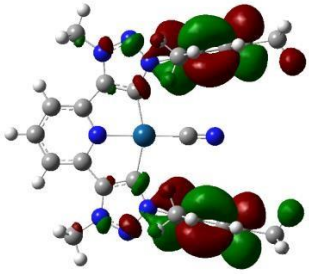
LUMO + 8 -0.08731



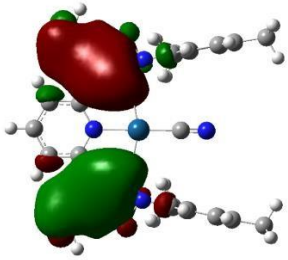
LUMO + 12 -0.05819



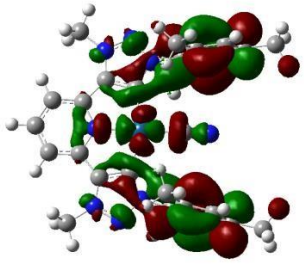
LUMO + 7 -0.09349



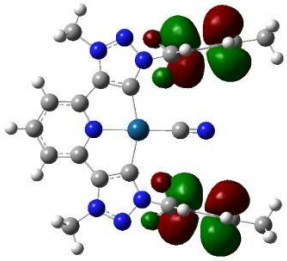
LUMO + 11 -0.06216



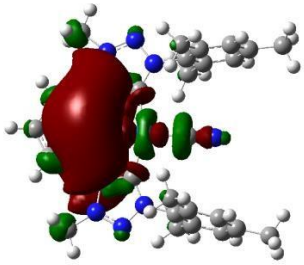
LUMO + 6 -0.09649



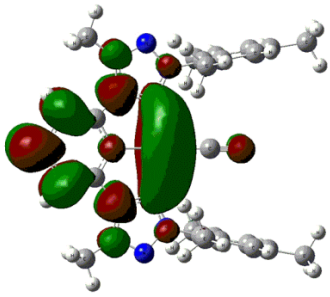
LUMO + 10 -0.07904



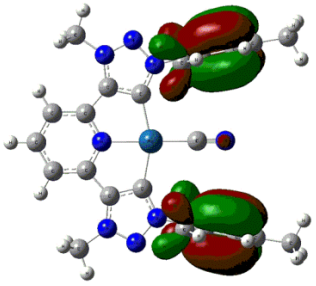
LUMO + 5 -0.09873



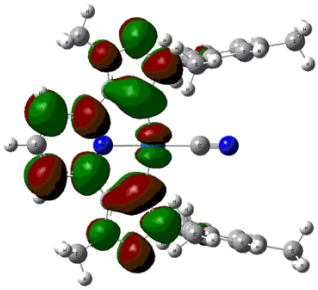
LUMO+4 -0.11373



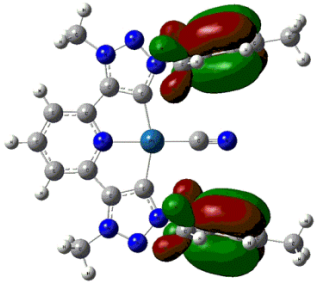
HOMO -0.31863



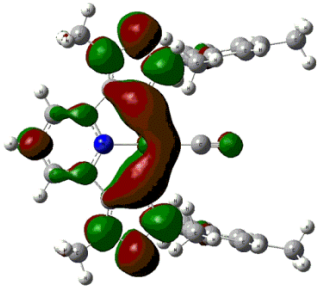
LUMO+3 -0.13984



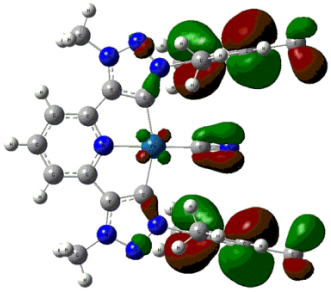
HOMO-1 -0.31882



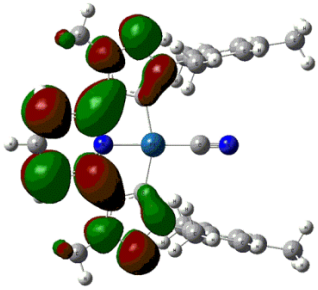
LUMO+2 -0.17378



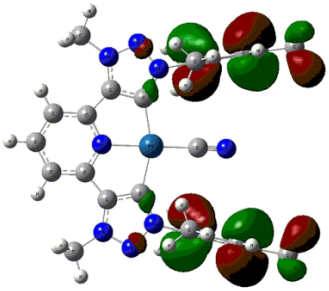
HOMO-2 -0.32153



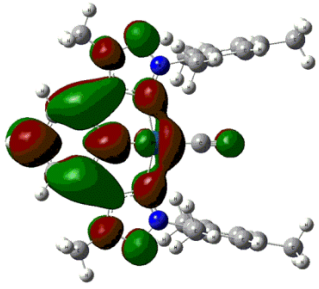
LUMO+1 -0.20150



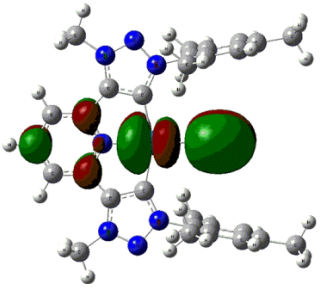
HOMO-3 -0.32233



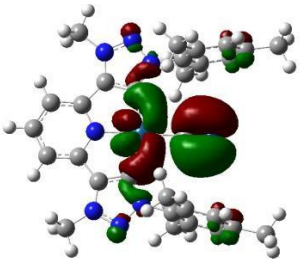
LUMO -0.20951



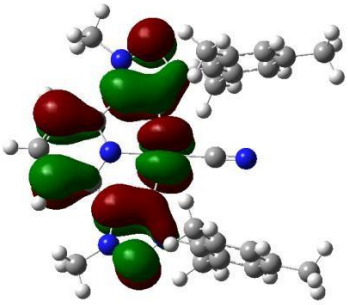
HOMO-4 -0.34085



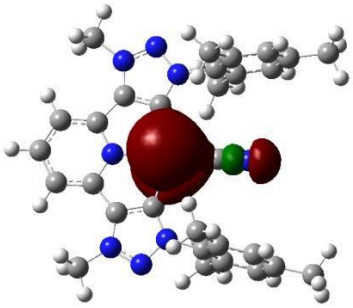
HOMO-5 -0.34119



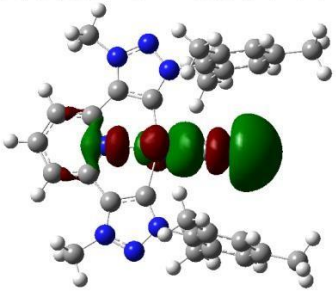
HOMO-6 -0.34260



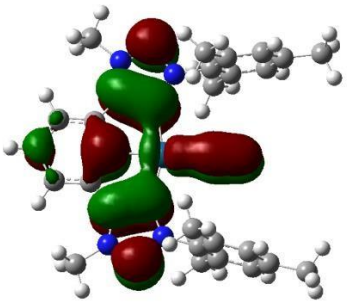
HOMO-7 -0.34794



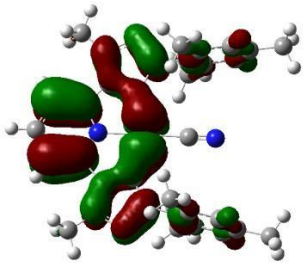
HOMO-8 -0.38122



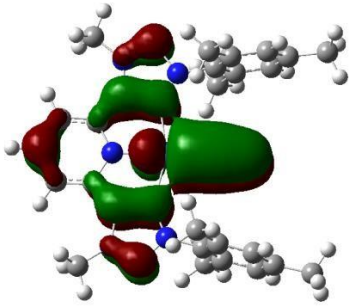
HOMO-9 -0.39430



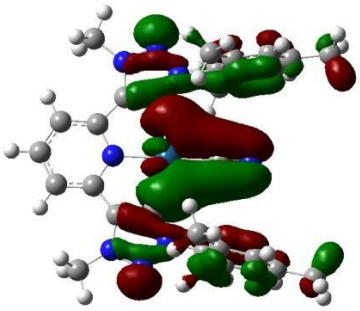
HOMO-10 -0.39856



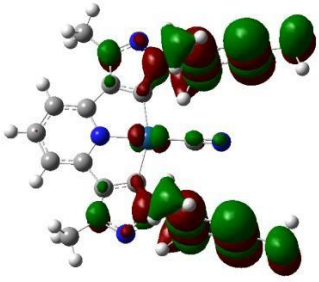
HOMO-11 -0.40939



HOMO-12 -0.41007



HOMO-13 -0.41475



HOMO-14 -0.41556

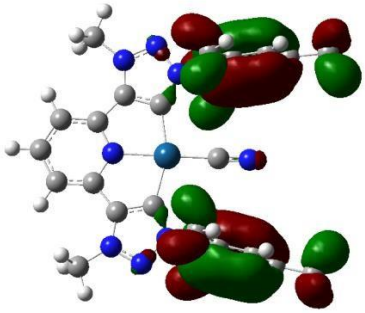


Table S3.1. TD-DFT assignment of electronic transitions along with oscillator strengths.

	λ (nm)	Excitation	Ocillatorstrength	Assignment
1	273	HOMO-9 → LUMO	0.1428	mixed ^{1}IL
	309–324	HOMO-6 → LUMO+1	0.0851	mixed ^{1}MLCT
	366–385	HOMO-4 →LUMO	0.0542	mixed ^{1}MLCT
2	263	HOMO-8 → LUMO	0.1751	mixed ^{1}IL
		HOMO-4 → LUMO+1	0.1905	mixed ^{1}IL
	315	HOMO-7 → LUMO (26%), HOMO-5 → LUMO (57%), HOMO-4 → LUMO+1 (13%)	0.0223	^{1}mixed MLCT
	365–410	HOMO-4 → LUMO	0.0103	^{1}mixed MLCT
3	264	HOMO-10 → LUMO	0.1548	mixed ^{1}IL
		HOMO-6 → LUMO+1	0.1177	mixed ^{1}MLCT
	362–414	HOMO-4 →LUMO	0.055	mixed ^{1}MLCT
4	245	HOMO-11, HOMO-8→ LUMO+1 and HOMO-9 →LUMO	0.2984	MP ^{1}IL CT
	290–350	HOMO-11 → LUMO+1 HOMO-6 → LUMO+2	0.0876	mixed ^{1}MLCT
	365–401	HOMO-6 → LUMO+1 HOMO- 1 → LUMO+2	0.0806	mixed ^{1}MLCT
5	243	H-7 to L +4; H-8 to L+1	0.2263	MP ^{1}IL CT
	286	HOMO -9 → LUMO HOMO-6 → LUMO +1 HOMO-4 → LUMP+2	0.0780	mixed ^{1}MLCT
	317	HOMO -6 → LUMO	0.1796	mixed ^{1}MLCT
6	227	HOMO -9 → L + 1 HOMO -4 → L + 3	0.4080	MP ^{1}IL CT
	260–300	HOMO -11 → LUMO; HOMO -9 → LUMO; HOMO -6 → L + 3: HOMO -9 → L + 1; HOMO - 6 → LUMO + 2	0.0351 0.1036	mixed ^{1}MLCT
	325	HOMO -4 → LUMO +2 HOMO -9 → LUMO +1; HOMO -6 → LUMO +2	0.0223 0.1036	mixed ^{1}MLCT

Table S3.2. Percentage weightages of HOMO and LUMO in **1**–**6**.

(a) For S_0 states of complexes bearing pyridine *bis*-imidazol-2-ylidene donors.

S_0	HOMO	LUMO
1		
Pincer ligand	58.27%	90.53%
Cl	32.01%	1.79%
Pt	9.72%	7.68%
2		
Pincer ligand	99.83%	90.58%
CH_3CN	0.12%	3.20%
Pt	0.05%	6.22%
3		
Pincer ligand	99.17%	91.91%
CN	0.57%	1.71%
Pt	0.26%	6.38%

(b) For S_0 states of complexes bearing triazol-5-ylidene donors.

S_0	HOMO	LUMO
4		
Pincer ligand	41.73%	93.08%
Cl	42.70%	1.28%
Pt	15.57%	5.64%
5		
Pincer ligand	99.86%	93.62%
CH_3CN	0.11%	2.25%
Pt	0.04%	4.13%
6		
Pincer ligand	98.08%	97.61%
CN	0.38%	0.52%
Pt	1.53%	1.87%