Unexpected structural preference with metallophilic Ag--- Au contacts in silver(I)-N heterocyclic carbene cluster; experimental and theoretical approach

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Table S1: Summary of key crystallographic data of **2** and **3.**

	2	**3**
Empirical formula	'$C_{65}H_{62}Ag_3F_{18}N_{19}P_3$'	'$C_{44.50}H_{45}Ag_2$ Au Cl F_{12} N_{13} $O_{0.50}$ P_2'
Formula weight	1867.85	1508.03
Crystal system	'trigonal'	'monoclinic'
Space group	'P-3 c 1'	'I12/m1'
Temperature (K)	100.01(10)	100.00(10)
Cell dimensions		
a (Å)	23.0541(3)	14.2719(4)
b (Å)	23.0541(3)	24.7697(6)
c (Å)	23.7591(4)	14.7213(4)
α(°)	90	90
β(°)	90	96.862(3)
γ(°)	120	90
Volume($Å^3$)	10936.0(3)	5166.9(2)
Z	6	4
Density (Mg m^{-3})	1.702	1.939
Absorption coefficient	0.965	3.789
F(000)	5598	2940
Theta range for data collection	1.9630-30.6820	3.7680-30.6130
Index ranges	-29<=h<=28,-31<=k<=32,-28<=l<= 30	-17<=h<=18,-32<=k<=32,-19<=l<= 18
Reflections collected	8104	5596
Independent reflections	9586	6503
GOF	1.023	1.050
Final R indices [I>2sigma(I)]	R1=0.0324, wR2=0.0760	R1=0.0427, wR2=0.0927
R indices (all data)	R1=0.0413, wR2=0.0813	R1=0.0529, wR2=0.0959

Table S2: Summary of selected bond distances (Å) of **2** and **3.** The theoretical values are obtained at B3LYP-D3/def2-TZVP (Ag, Au), 6-31G** (C, H, N, Cl) level of theory.[1,2,3]

	2			**3**	
	Experimental	Theoretical		Experimental	Theoretical
Ag(1)-Ag(1)	2.7725(3)	2.8856	Au(1)-Ag(1)	3.1006(4)	3.5003
Ag(2)-Ag(2)	2.7539(3)	2.8848	Ag(1)-Cl(1)	2.5476(10)	2.6340
Ag(1)-C(12)	2.257(2)	2.3137	Au(1)-C(10)	2.036(5)	2.0582
Ag(1)-N(1)	2.3281(18)	2.3769	Ag(1)-N(1)	2.240(4)	2.2969
Ag(1)-N(5)	2.3294(18)	2.3769	Ag(1)-N(5)	2.229(4)	2.2767

Table S3: Summary of selected bond angles (°)of **2** and **3**.The theoretical values are obtained at B3LYP-D3/def2-TZVP (Ag, Au), 6-31G** (C, H, N, Cl) level of theory.

	2			**3**	
	Experimental	Theoretical		Experimental	Theoretical
Ag(1)-Ag(1)-Ag(1)	60.0	60.01	Ag(1)-Au(1)-Ag(1)	66.136(13)	60.33
Ag(1)-C(12)-Ag(1)	52.01(5)	51.34	Ag(1)-Cl(1)-Ag(1)	83.22(4)	83.79
Ag(1)-C(12)-Ag(1)	52.53(5)	51.45	Cl(1)-Ag(1)-Au(1)	105.32(2)	176.57
C(12)-Ag(1)-Ag(1)	112.48(5)	111.50	Ag(1)-Au(1)-C(10)	60.46(11)	59.20
C(12)-Ag(1)-Ag(1)	111.96(5)	111.29	Ag(1)-Au(1)-C(10)	126.58(11)	117.42
C(12)-Ag(1)-C(12)	163.84(7)	162.94	C(10)-Au(1)-C(10)	173.0(2)	176.57
N(1)-Ag(1)-Ag(1)	117.22(5)	113.10	N(1)-Ag(1)-Au(1)	98.50(9)	71.72
N(1)-Ag(1)-Ag(1)	125.21(5)	123.37	N(1)-Ag(1)-Cl(1)	110.02(9)	112.11
C(12)-Ag(1)-N(1)	99.80(7)	103.78	N(1)-Ag(1)-N(5)	126.64(14)	152.92
C(12)-Ag(1)-N(1)	85.92(7)	85.72	N(5)-Ag(1)-Au(1)	101.68(9)	97.77

N(1)-Ag(1)-N(5)	105.76(7)	114.09	N(5)-Ag(1)-Cl(1)	111.24(9)	94.79
N(4)-C(12)-N(3)	103.45(18)	103.63	N(4)-C(10)-N(3)	104.7(4)	104.39
N(5)-Ag(1)-Ag(1)	115.22(5)	113.13			
N(5)-Ag(1)-Ag(1)	128.70(5)	123.36			
C(12)-Ag(1)-N(5)	107.86(7)	103.64			
C(12)-Ag(1)-N(5)	85.27(7)	85.73			

Table S4: Vertical electronic transition as computed at TD-DFT $SMD_{(acetonitrile)}$ B3LYP-D3/def2-TZVP (Ag), 6-31G** (C, H, N) level of theory for complex **2.**

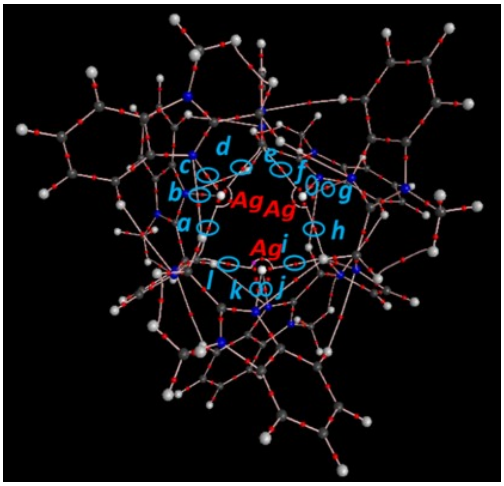
E_e (eV)	λ_{theo} (nm)	Osc. Strength (*f*)	Key transitions
4.1055	301.99	0.1065	HOMO→LUMO
4.1106	301.62	0.1073	HOMO-1→LUMO
4.1291	300.27	0.0135	HOMO-2→LUMO
4.3981	281.91	0.0100	HOMO-1→LUMO+3
4.5208	274.25	0.0111	HOMO→LUMO+5
4.5593	271.94	0.0580	HOMO→LUMO-4
4.5596	271.92	0.0589	HOMO-1→LUMO+4
4.7064	263.44	0.0191	HOMO-3→LUMO
4.7068	263.41	0.0198	HOMO-4→LUMO

Table S5: Vertical electronic transition as computed at TD-DFT $SMD_{(acetonitrile)}$ B3LYP-D3/def2-TZVP (Ag, Au), 6-31G** (C, H, N, Cl) level of theory for complex **3.**

E_e (eV)	**λ_{theo} (nm)**	**Osc. Strength (*f*)**	**Key transitions**
4.1471	298.97	0.0133	HOMO→LUMO
4.4537	278.39	0.0102	HOMO-2→LUMO
4.4765	276.96	0.0181	HOMO-5→LUMO
4.5639	271.66	0.0366	HOMO→LUMO+1
4.6676	265.63	0.0206	HOMO-12→LUMO
4.6951	264.07	0.2297	HOMO-11→LUMO
4.7123	263.11	0.0181	HOMO-1→LUMO+1
4.7411	261.51	0.0382	HOMO-3→LUMO+1
4.7509	260.97	0.0331	HOMO-10→LUMO+1
4.7770	259.54	0.0517	HOMO-9→LUMO+1
4.7998	258.31	0.0384	HOMO-8→LUMO
4.8151	257.49	0.0174	HOMO-7→LUMO

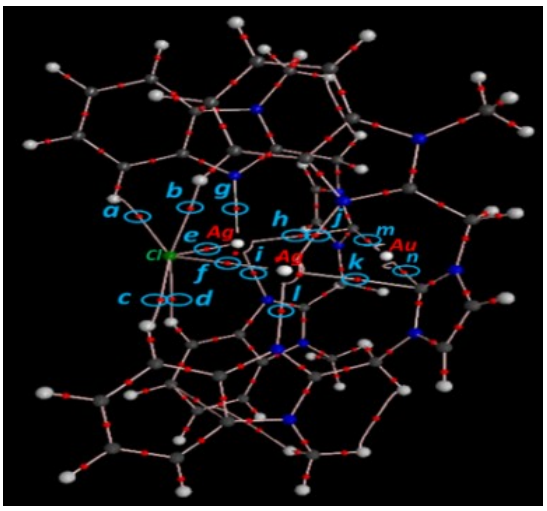
Table S6: Estimated strengths in complex **2** and complex **3** through the bond critical point (ρ) in a.u. The topological parameters are derived from Atoms-in-Molecules (AIM) analysis on optimized geometry computed at the B3LYP-D3/def2-TZVP (Ag, Au), 6-31G** (C, H, N) level of theory.

Ag-Ag-Ag



	ρ	$\nabla^2\rho$	G	V=1/4$\nabla^2\rho$-2G	E=1/2(V)	E (kcal/mol)
a	0.065	-0.044	0.057	-0.125	-0.062	-38.9
b	0.050	-0.053	0.054	-0.121	-0.060	-37.6
c	0.050	-0.053	0.054	-0.121	-0.060	-37.6
d	0.065	-0.044	0.057	-0.125	-0.062	-38.9
e	0.065	-0.044	0.057	-0.125	-0.062	-38.9
f	0.049	-0.052	0.054	-0.121	-0.060	-37.6
g	0.049	-0.053	0.054	-0.121	-0.060	-37.6
h	0.065	-0.045	0.057	-0.125	-0.062	-38.9
i	0.065	-0.044	0.057	-0.125	-0.062	-38.9
j	0.050	-0.053	0.055	-0.123	-0.061	-38.3
k	0.050	-0.053	0.055	-0.123	-0.061	-38.3
l	0.065	-0.044	0.057	-0.125	-0.062	-38.9
Total Energy						-460.4

Ag-Ag-Au



	ρ	$\nabla^2\rho$	G	$V=1/4\nabla^2\rho-2G$	E=1/2(V)	E (kcal/mol)
a	0.007	-0.006	0.005	-0.011	-0.005	-3.1
b	0.013	-0.010	0.009	-0.020	-0.01	-6.3
c	0.007	-0.006	0.005	-0.011	-0.005	-3.1
d	0.013	-0.010	0.009	-0.020	-0.01	-6.3
e	0.043	-0.036	0.040	-0.089	-0.044	-27.6
f	0.043	-0.036	0.040	-0.089	-0.044	-27.6
g	0.061	-0.067	0.071	-0.159	-0.079	-49.6
h	0.015	-0.011	0.010	-0.023	-0.011	-6.9
i	0.057	-0.064	0.067	-0.15	-0.075	-47.1
j	0.057	-0.064	0.067	-0.15	-0.075	-47.1
k	0.015	-0.011	0.010	-0.023	-0.011	-6.9
l	0.061	-0.067	0.071	-0.159	-0.079	-49.6
m	0.133	-0.054	0.119	-0.251	-0.125	-78.4
n	0.133	-0.054	0.119	-0.251	-0.125	-78.4
Total Energy						-438.0

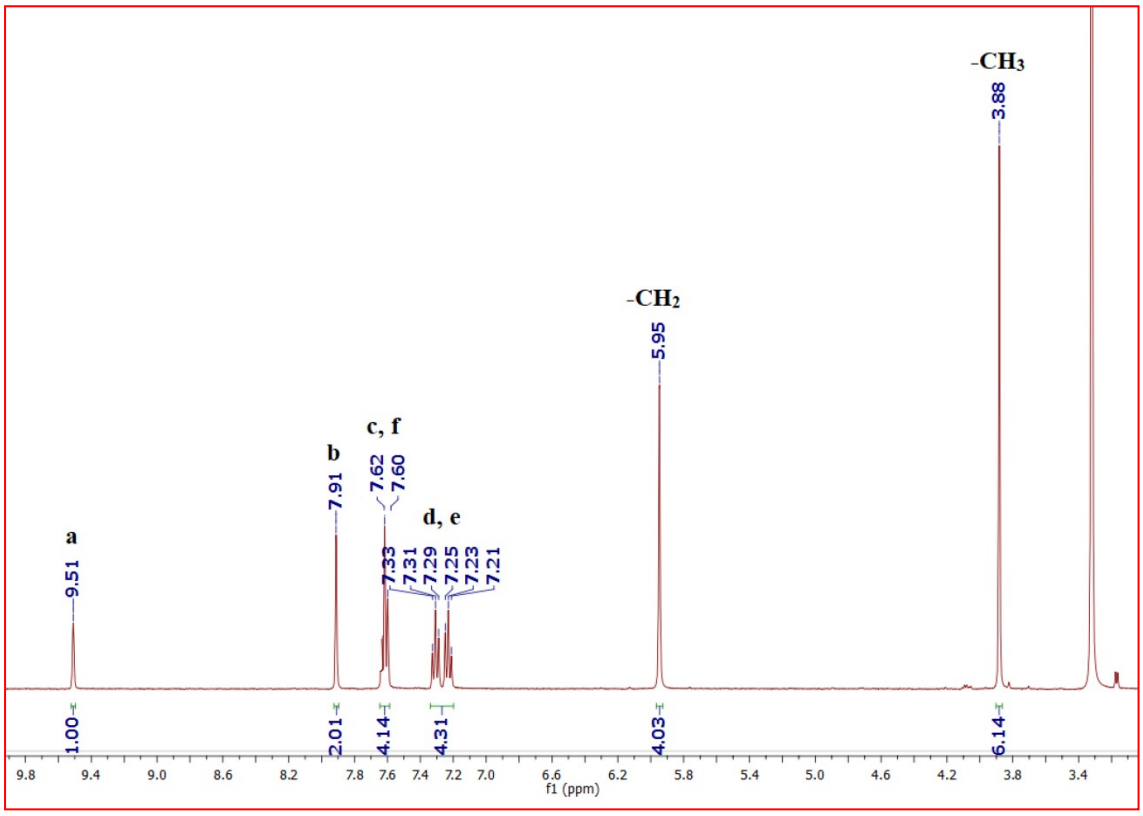


Figure S1: ^{1}HNMR spectra of **1**.HPF_6.

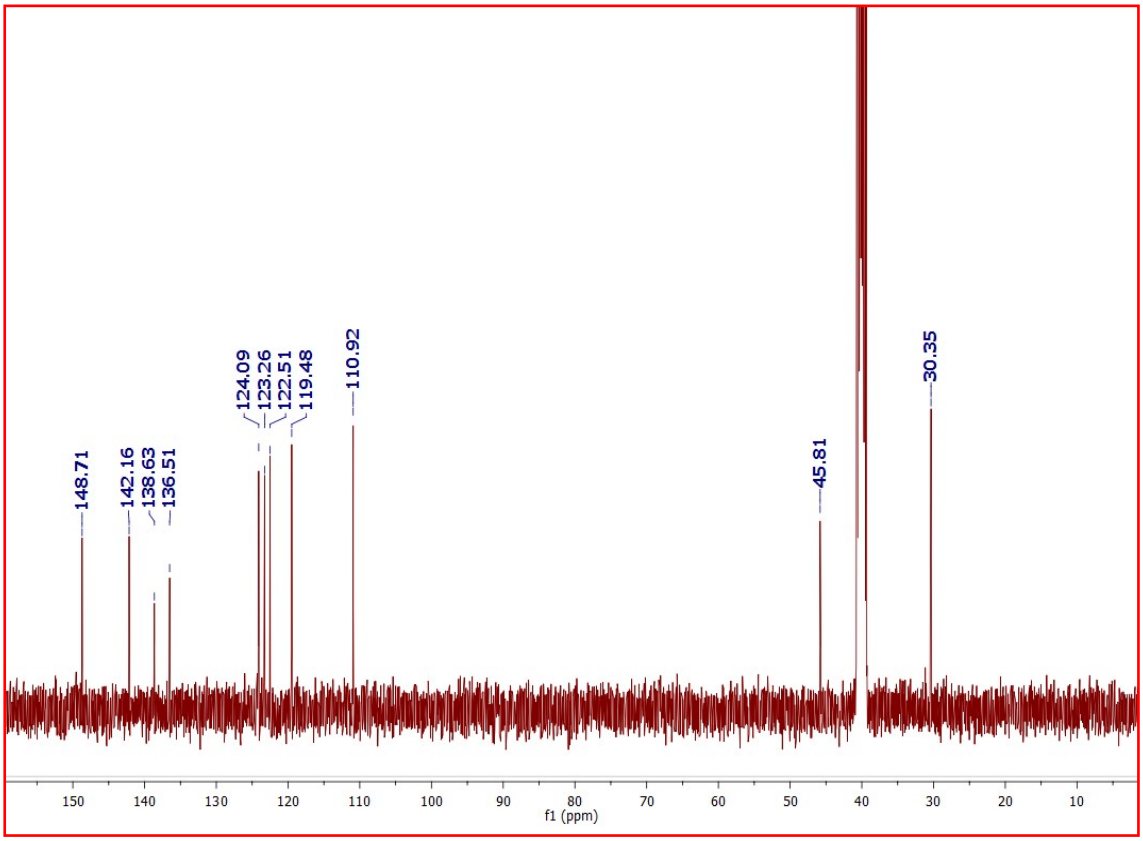


Figure S2: ^{13}CNMR spectra of **1**.HPF_6.

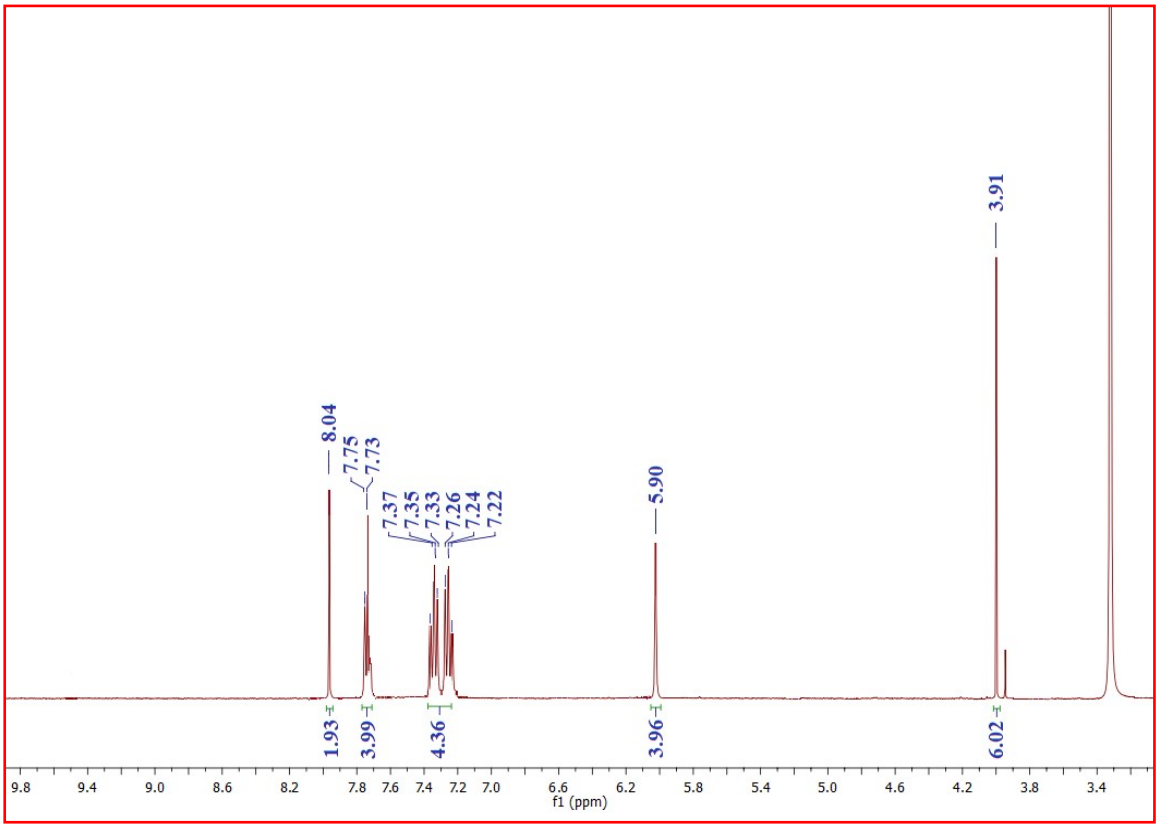


Figure S3: ^{1}H NMR spectra of complex **2**.

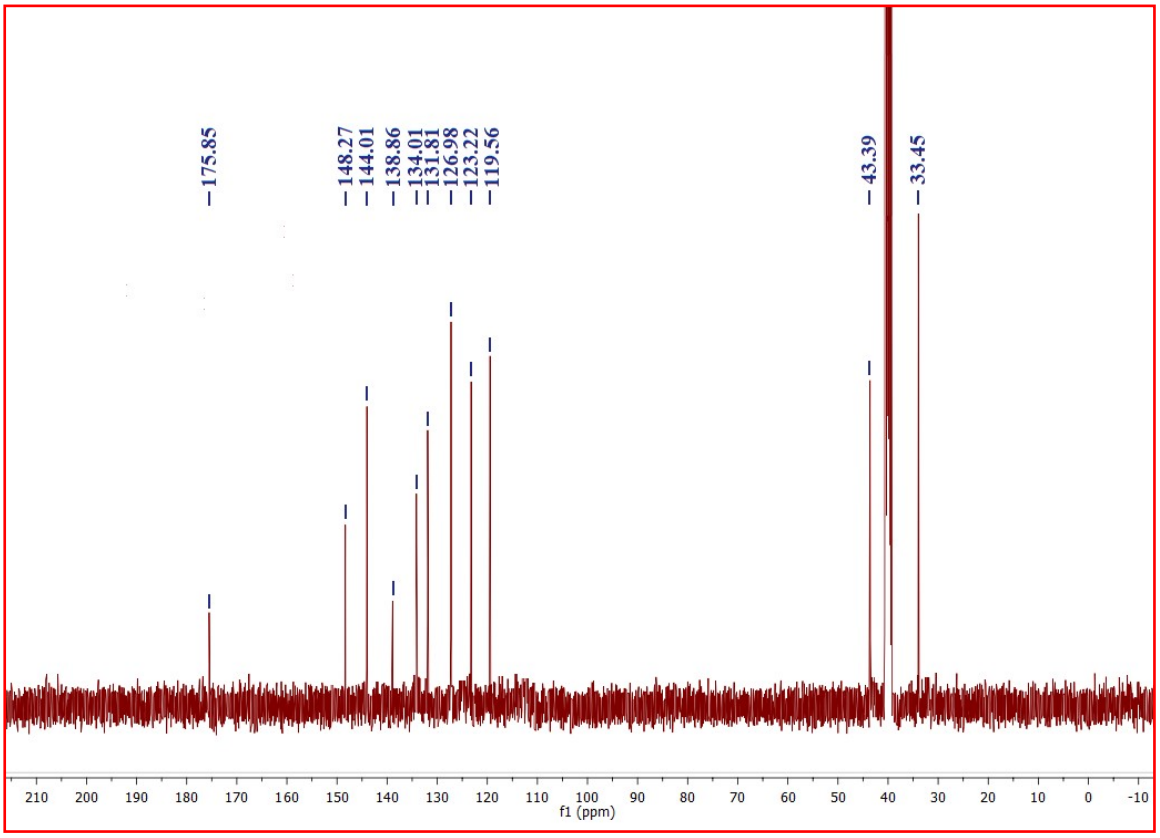


Figure S4: ^{13}C NMR spectra of complex **2**.

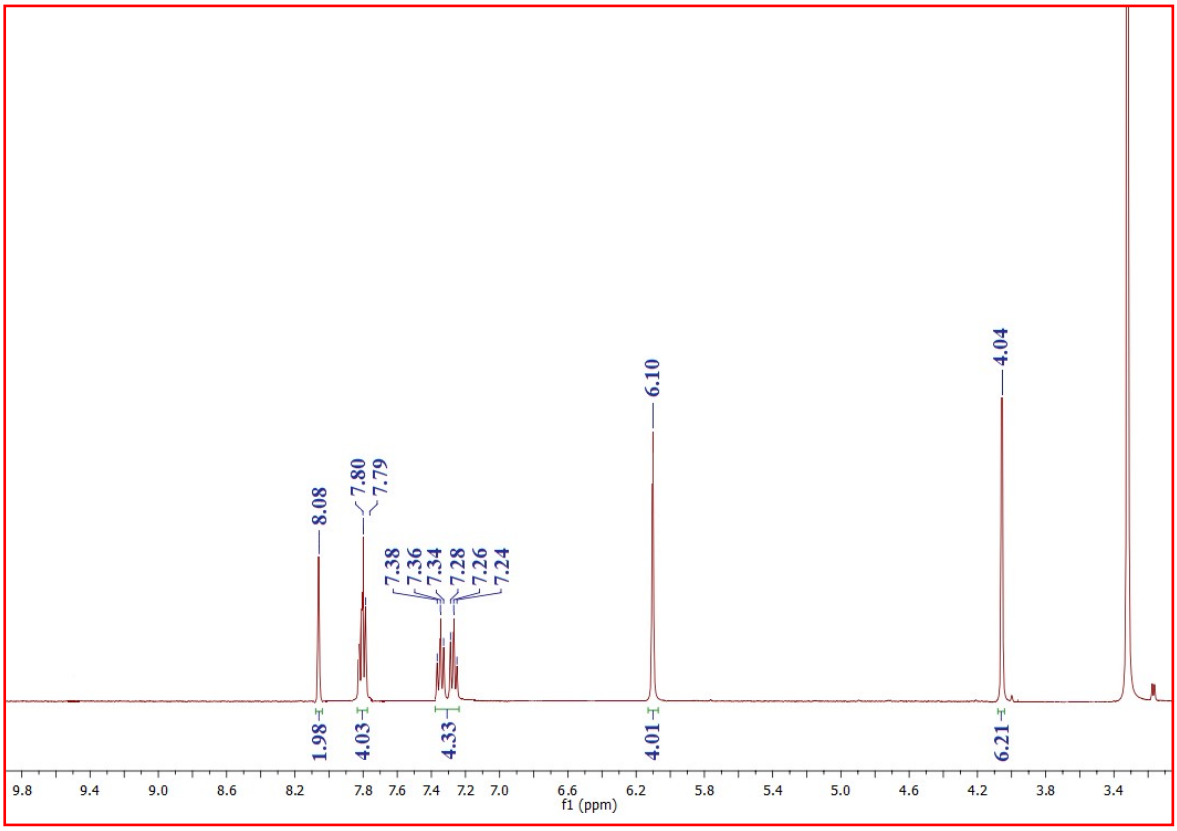


Figure S5: ^{1}H NMR spectra of complex **3**.

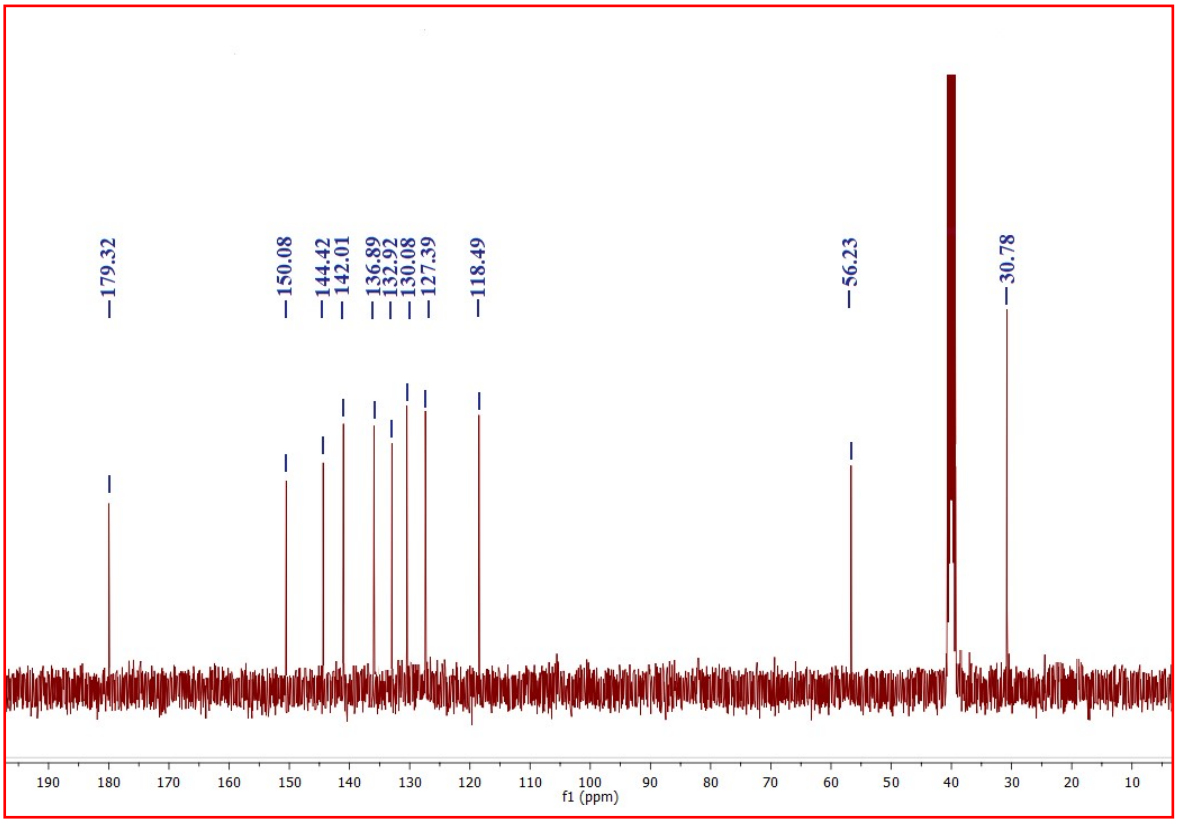


Figure S6: ^{13}C NMR spectra of complex **3**.

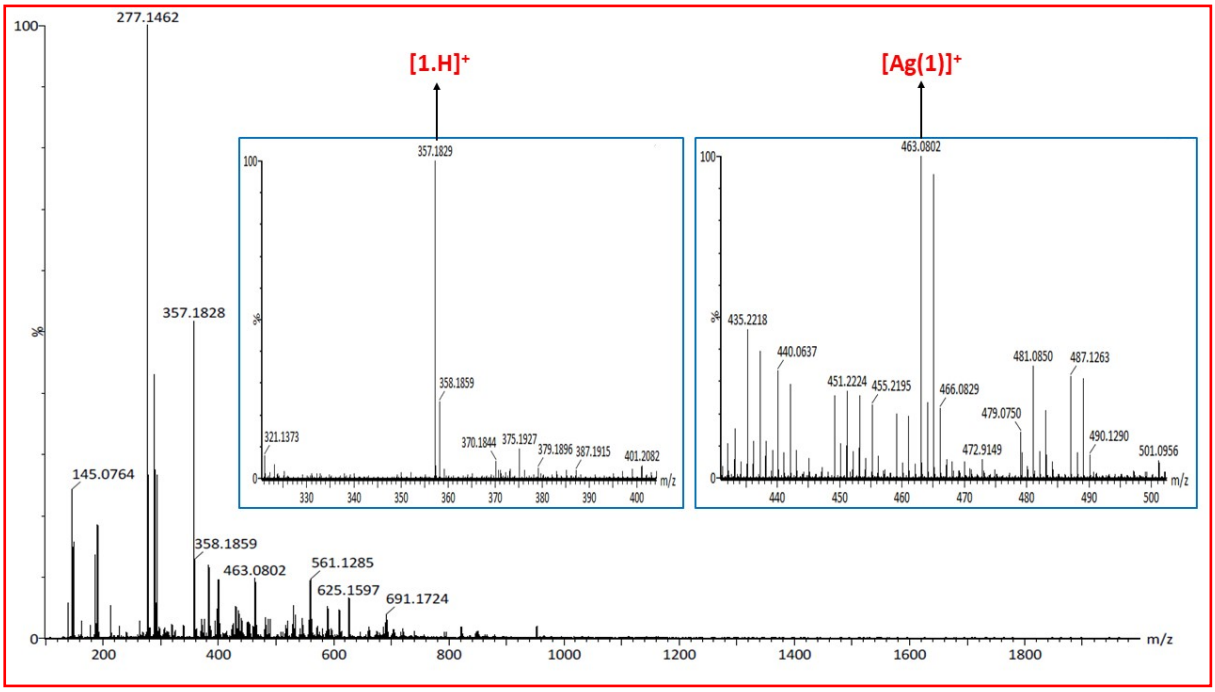


Figure S7:HR-MS spectra of complex **2**.

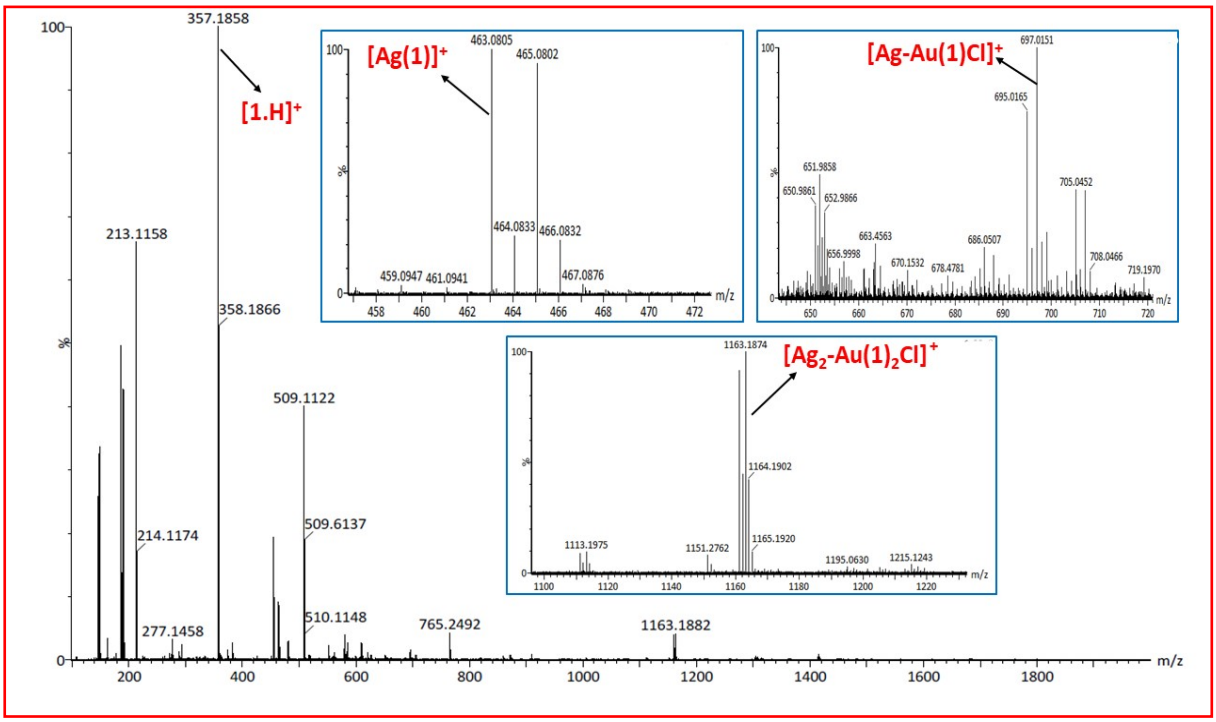


Figure S8:HR-MS spectra of complex **3**.

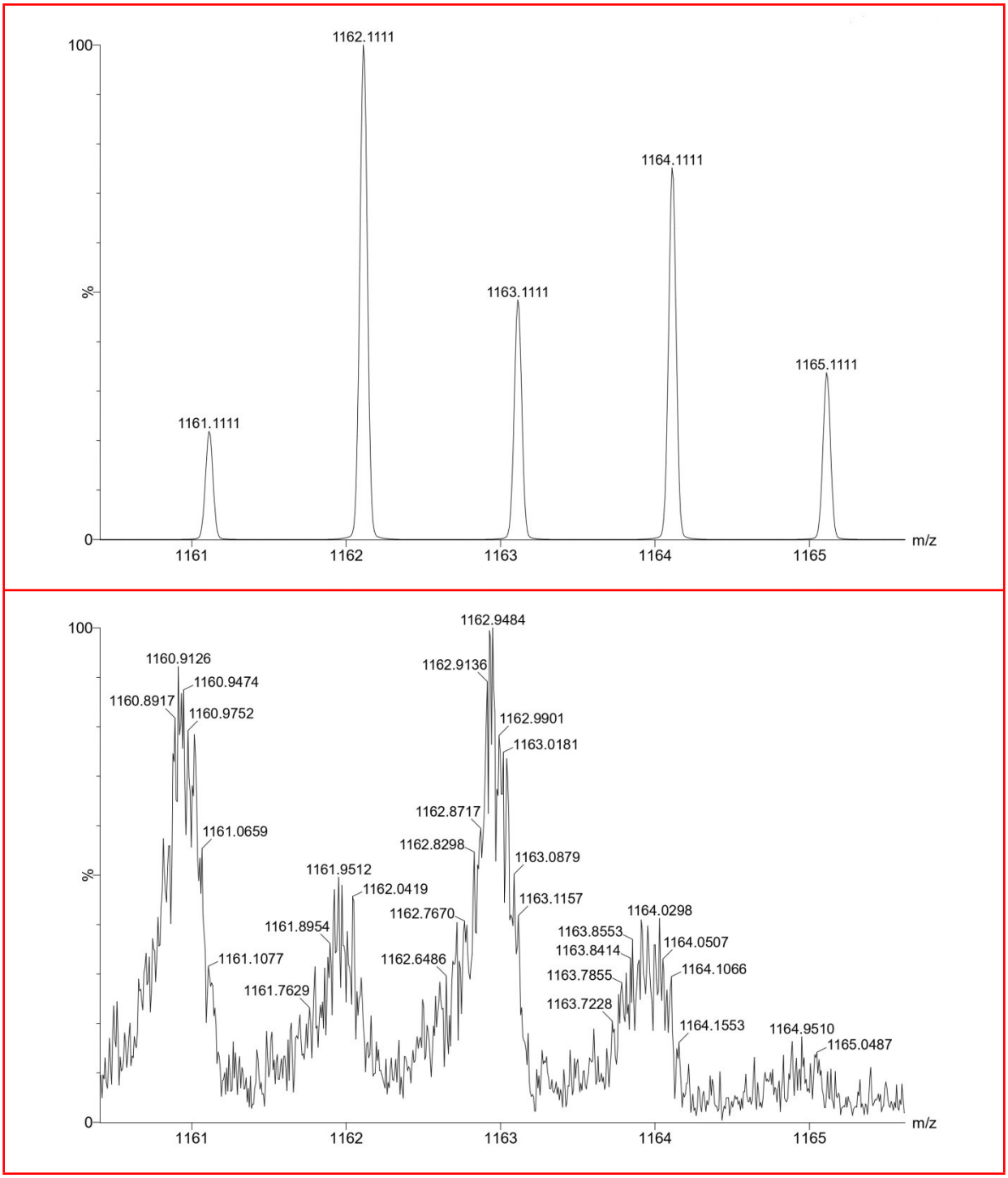


Figure S9: Mass spectrometry: experimental data (top) and isotopic pattern simulations (bottom) of complex **3**.

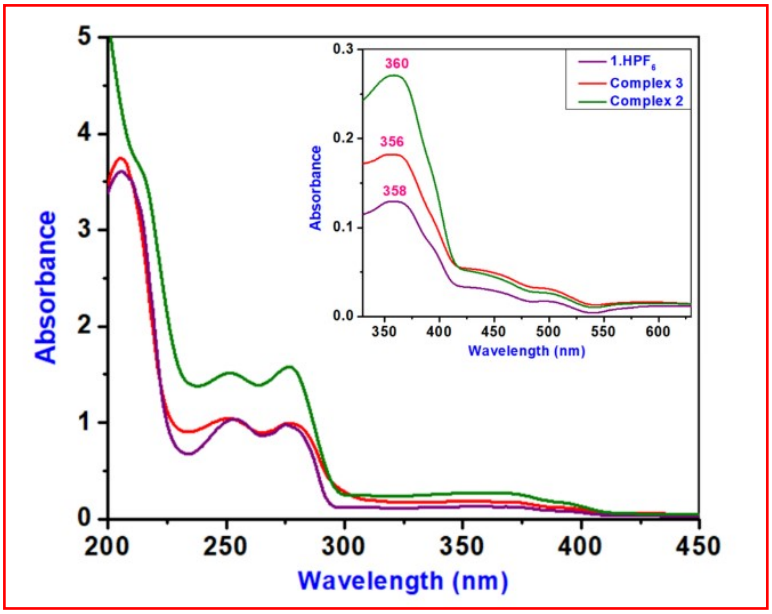
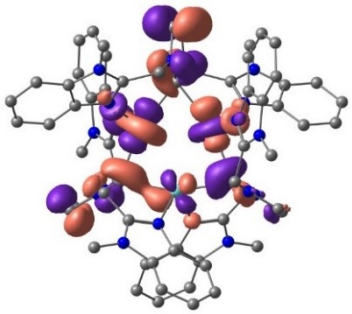
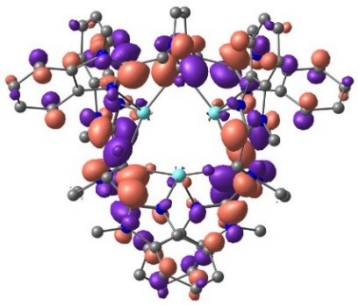


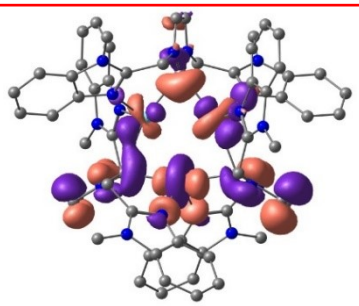
Figure S10: UV-Vis spectra of **1.**HPF_6, complex **2,** and complex **3** at 0.05 mM conc. at room temperature.



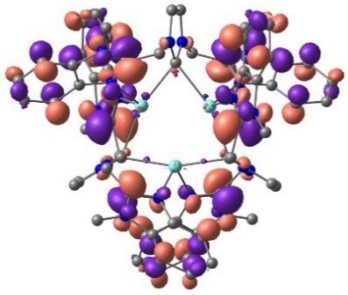
HOMO (E=-5.9041 eV)



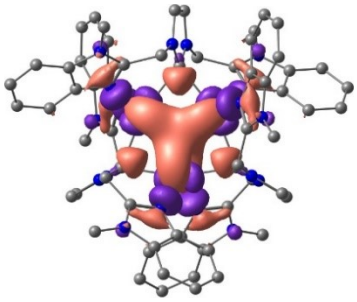
LUMO (E=-1.1633 eV)



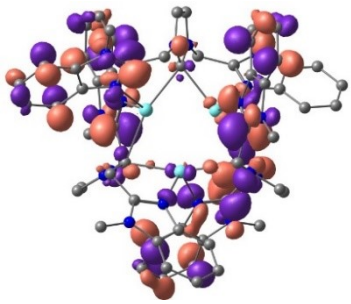
HOMO-1 (E=-5.9087 eV)



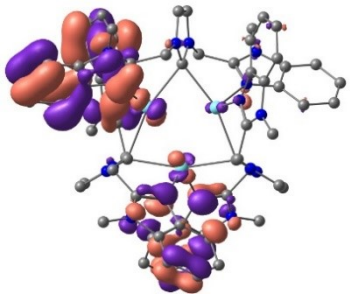
LUMO+1 (E=-0.9453 eV)



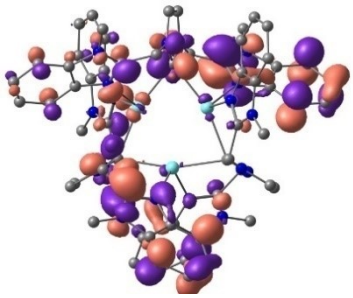
HOMO-2 (E=-6.0290 eV)



LUMO+2 (E=-0.9333 eV)

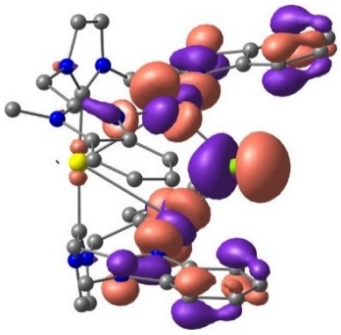
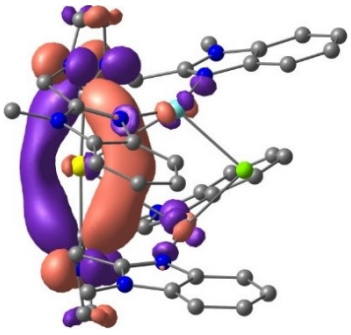
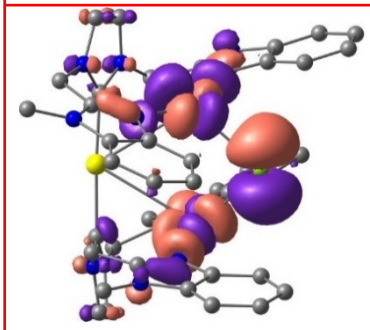
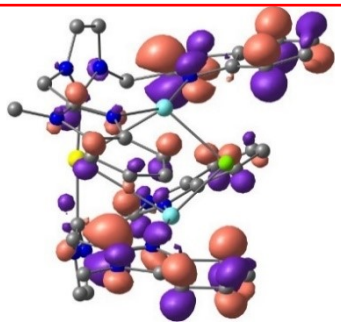


HOMO-3 (E=-6.3623 eV)



LUMO+3 (E=-0.9328 eV)

Figure S11. Molecular orbitals obtained for **2** at TD-DFT $SMD_{(acetonitrile)}$ / B3LYP-D3/def2-TZVP (Ag), 6-31G** (C, H, N) level of theory.

	
HOMO (E=-6.1158 eV)	**LUMO** (E=-1.3187 eV)
	
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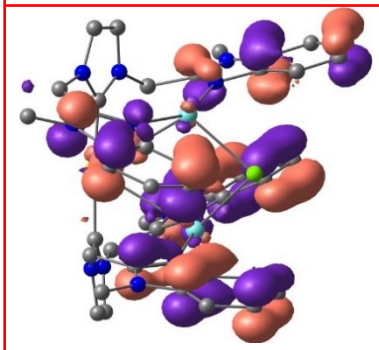
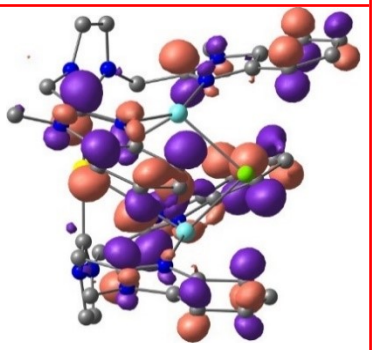
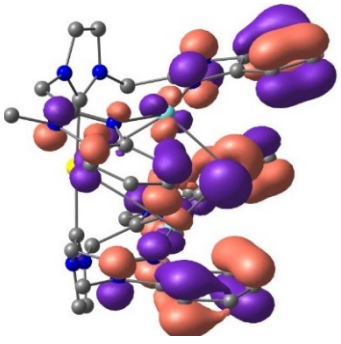
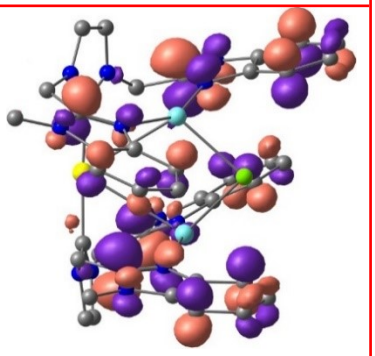
	
HOMO-2 (E= -6.2502 eV)	**LUMO+2** (E=-0.8329 eV)
	
HOMO-3 (E= -6.2589 eV)	**LUMO+3** (E= -0.7461 eV)

Figure S12. Molecular orbitals obtained for **3**at TD-DFT $SMD_{(acetonitrile)}$ / B3LYP-D3/def2-TZVP (Ag, Au), 6-31G** (C, H, N, Cl) level of theory.

References:

1. S. Grimme, J. Antony, S. Ehrlich andH. Krieg, *J. Chem. Phys.*,2010, **132**, 154104−154119.
2. F. Weigend andR. Ahlrichs,*Phys. Chem. Chem. Phys.*,2005,**7**, 3297– 3305.
3. V. A. Rassolov, J. A.Pople, M. A. Ratner andT. Windus, *J. Chem. Phys.*,1998,**109**, 1223−1229.