SUPPORTING INFORMATION

Metallophilic Au(I)···M(I) Interactions (M = Tl, Ag) in Heteronuclear Complexes with 1,4,7-Triazacyclononane: Structural Features and Optical Properties

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Table S1. Selected bond lengths [Å] and angles [°] for {[{Au(C$_6$Cl$_5$)$_2$}Tl(TACN)]$_2$}$_n$ (1)

Tl(1)-Au(1)	3.3377(6)	Au(1)-C(1)	2.056(9)
Tl(1)-Au(2)	3.5478(6)	Au(2)-C(7)	2.039(9)
Tl(1)-N(1)	2.663(8)	Tl(1)-Cl(10)#2	3.6366(5)
Tl(1)-N(2)	2.614(9)	Tl(1)-Cl(3)#4	3.6923(5)
Tl(1)-N(3)	2.671(9)		

Au(1)-Tl(1)-Au(2)	144.29(1)	N(1)-Tl(1)-Au(1)	70.01(16)
C(1)-Au(1)-C(1)#1	180.0	N(3)-Tl(1)-Au(1)	126.63(17)
Tl(1)-Au(1)-Tl(1)#1	180.0	N(2)-Tl(1)-Au(2)	72.66(18)
C(7)-Au(2)-C(7)#2	180.0	N(1)-Tl(1)-Au(2)	136.86(16)
Tl(1)-Au(2)-Tl(1)#2	180.0	N(3)-Tl(1)-Au(2)	89.08(17)
N(2)-Tl(1)-N(1)	65.4(2)	C(1)-Au(1)-Tl(1)	93.4(2)
N(2)-Tl(1)-N(3)	66.3(3)	C(1)-Au(1)-Tl(1)#1	86.6(2)
N(1)-Tl(1)-N(3)	65.7(2)	C(7)-Au(2)-Tl(1)	97.2(3)
N(2)-Tl(1)-Au(1)	118.61(19)	C(7)-Au(2)-Tl(1)#2	82.8(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1   #2 -x+1,-y+1,-z+2   #4 -x+1,-y+2,-z+1

Table S2. Hydrogen bonds for {[{Au(C$_6$Cl$_5$)$_2$}Tl(TACN)]$_2$}$_n$ (1).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Au(1)	0.99	2.9315(4)	3.4867(4)	129.1
C(16)-H(16A)...Au(2)	0.99	3.0261(5)	3.8534(4)	141.8
N(1)-H(1)...Cl(8)#1	1.00	2.89	3.460(4)	116.9
N(2)-H(2)...Cl(5)#2	1.00	2.85	3.458(4)	119.6
N(3)-H(3)...Cl(9)#3	1.00	2.88	3.678(4)	137.3
N(3)-H(3)...Cl(10)#3	1.00	2.83	3.644(4)	138.9
C(15)-H(15B)...Cl(6)#4	0.99	2.87	3.717(5)	144.3
C(17)-H(17A)...Cl(2)#4	0.99	2.98	3.735(5)	134.3
C(17)-H(17B)...Cl(9)#3	0.99	2.95	3.738(5)	137.2
C(18)-H(18B)...Cl(8)#1	0.99	2.94	3.563(5)	122.0

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1   #2 -x+1,-y+1,-z+2   #3 -x+2,-y+1,-z+   #4 -x+2,-y,-z+2

#5 -x+2,-y+1,-z+2   #6 -x+1,-y+2,-z+1   #7 x,y+1,z

Table S3. Selected bond lengths [Å] and angles [°] for [{Au(C$_6$Cl$_5$)$_2$}Ag(TACN)] (3)

Au(1)-Ag(1)	2.6915(4)	Ag(1)-C(1)	2.398(4)
Ag(1)-N(1)	2.429(4)	Au(1)-C(1)	2.081(4)
Ag(1)-N(2)	2.365(4)	Au(1)-C(7)	2.035(4)
Ag(1)-N(3)	2.386(4)		
C(1)-Au(1)-C(7)	176.62(17)	N(2)-Ag(1)-Au(1)	129.07(10)
C(1)-Au(1)-Ag(1)	58.68(12)	N(2)-Ag(1)-N(3)	76.05(14)
C(7)-Au(1)-Ag(1)	124.70(13)	N(2)-Ag(1)-C(1)	160.06(15)
N(1)-Ag(1)-Au(1)	142.92(10)	N(3)-Ag(1)-Au(1)	133.09(10)
N(1)-Ag(1)-C(1)	99.50(14)	N(3)-Ag(1)-N(1)	74.99(14)
N(1)-Ag(1)-N(2)	74.40(14)	N(3)-Ag(1)-C(1)	121.34(14)
C(1)-Ag(1)-Au(1)	47.83(10)		

Table S4. Hydrogen bonds for [{Au(C$_6$Cl$_5$)$_2$}Ag(TACN)] (3).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Cl(8)#1	1.00	2.89	3.460(4)	116.9
N(2)-H(2)...Cl(5)#2	1.00	2.85	3.458(4)	119.6
N(3)-H(3)...Cl(9)#3	1.00	2.88	3.678(4)	137.3
N(3)-H(3)...Cl(10)#3	1.00	2.83	3.644(4)	138.9
C(15)-H(15B)...Cl(6)#4	0.99	2.87	3.717(5)	144.3
C(17)-H(17A)...Cl(2)#4	0.99	2.98	3.735(5)	134.3
C(17)-H(17B)...Cl(9)#3	0.99	2.95	3.738(5)	137.2
C(18)-H(18B)...Cl(8)#1	0.99	2.94	3.563(5)	122.0

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z+1   #2 -x+1,-y,-z+1   #3 -x+1,-y+1,-z+1   #4 x-1,y,z

Table S5. Selected bond lengths [Å] and angles [°] for [{Au(C₆F₅)₂}{Ag(TACN)}₂Au(C₆F₅)₂] (4).

Au(1)-Ag(1)	2.7331(9)	Au(1)-C(1)	2.087(9)
Au(1)-Au(2)	3.4022(9)	Au(2)-C(7)	2.048(9)
Ag(1)-N(1)	2.324(8)	Ag(1)-C(1)#1	2.359(9)
Ag(1)-N(2)	2.411(8)	Ag(1)-F(10)#2	3.095(6)
Ag(1)-N(3)	2.464(8)		

C(1)-Au(1)-C(1)#1	178.6(5)	N(2)-Ag(1)-N(3)	73.2(3)
C(1)-Au(1)-Ag(1)#1	56.7(3)	N(1)-Ag(1)-Au(1)	119.49(19)
C(1)-Au(1)-Ag(1)	124.3(3)	C(1)#1-Ag(1)-Au(1)	47.7(2)
C(1)#1-Au(1)-Ag(1)	56.7(3)	N(2)-Ag(1)-Au(1)	164.79(19)
Ag(1)#1-Au(1)-Ag(1)	110.33(4)	N(3)-Ag(1)-Au(1)	106.93(19)
C(7)-Au(2)-C(7)#1	179.0(5)	N(1)-Ag(1)-F(10)#1	91.1(2)
N(1)-Ag(1)-C(1)#1	166.2(3)	C(1)#1-Ag(1)-F(10)#1	89.3(3)
N(1)-Ag(1)-N(2)	75.5(3)	N(2)-Ag(1)-F(10)#1	71.4(2)
C(1)#1-Ag(1)-N(2)	117.6(3)	N(3)-Ag(1)-F(10)#1	144.2(2)
N(1)-Ag(1)-N(3)	74.8(3)	Au(1)-Ag(1)-F(10)#1	108.68(12)
C(1)#1-Ag(1)-N(3)	112.1(3)		

Symmetry transformations used to generate equivalent atom:

#1 -x+1,y,-z+1/2   #2 -x+1,y-1,-z+1/2

Table S6. Hydrogen bonds for [{Au(C$_6$F$_5$)$_2$}{Ag(TACN)}$_2$Au(C$_6$F$_5$)$_2$] (4).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(15)-H(15B)...Au(2)#1	0.99	2.8010(3)	3.5941(4)	137.5
N(2)-H(2)...F(3)#2	1.00	2.2239(2)	3.2209(3)	174.8
N(3)-H(3)...F(5)#1	1.00	2.56	3.172(10)	119.2
N(3)-H(3)...F(6)	1.00	2.56	3.267(10)	127.3
C(14)-H(14B)...F(2)#3	0.99	2.49	3.350(11)	144.8
C(15)-H(15B)...F(5)#4	0.99	2.53	3.226(11)	127.3
C(17)-H(17A)...F(8)#5	0.99	2.62	3.260(11)	122.3

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2   #2 x+1/2,y+1/2,z   #3 -x+1,-y+2,-z+1

#4 -x+1,y+1,-z+1/2   #5 x+1/2,y-1/2,z

Table S7. Population analysis (%) for the model system **1a.**

Model 1a	Tl	Au	L$_5$	C$_6$Cl$_5$
LUMO+6	10,2	3,84	2,31	83,44
LUMO+5	36,8	25,15	5,47	30,22
LUMO+4	33,16	18,83	1,51	46,26
LUMO+3	42,47	12,62	14,6	29,67
LUMO+2	10,7	20,59	0,79	67,7
LUMO+1	11,66	23,66	0,65	59,35
LUMO	37,35	26	4,18	32,08
HOMO	30,58	47,96	10,56	10,85
HOMO-1	23,15	40,79	13,93	22
HOMO-2	10,61	27,08	5,16	57,08
HOMO-3	1,22	2,28	0,56	95,75
HOMO-4	25,22	31,05	23,21	19,61
HOMO-5	6,37	5,89	6,88	80,64
HOMO-6	3,68	5,22	1,63	89,41
HOMO-7	1,52	19,73	1,66	74,93
HOMO-8	9,53	20,88	32,44	36,83

Table S8. Population analysis (%) for the model system **3a.**

Model 3a	Au	Ag	L$_5$	C$_6$Cl$_5$
LUMO+3	24	58	1	17
LUMO+2	6	13	1	81
LUMO+1	9	12	1	78
LUMO	18	17	3	62
HOMO	19	33	22	26
HOMO-1	13	5	5	77
HOMO-2	1	1	0	98
HOMO-3	24	27	27	21
HOMO-4	42	20	19	19
HOMO-5	1	2	1	97
HOMO-6	17	20	12	51

Table S9. Population analysis (%) for the model system **4a**

Model 4a	Au$_A$	Ag	L$_5$	(C6F5)$_A$	Au$_B$	(C$_6$F$_5$)$_B$
LUMO+2	1	43	1	1	54	0
LUMO+1	1	20	9	49	21	1
LUMO	3	32	4	14	45	2
HOMO	26	20	5	13	28	9
HOMO-1	9	21	12	14	6	38
HOMO-2	28	5	3	9	2	53
HOMO-3	4	26	17	9	8	36
HOMO-4	6	3	1	4	6	80

Table S10. TD-DFT first Singlet-Singlet Excitation Calculations for model system **1a**.

Model	exc.	λ_{calc} (nm)	f (s)	contributions
1a	$S_0 \to S_1$	363	0.2748	HOMO → LUMO (47)
	$S_0 \to S_2$	332	0.0218	HOMO-1 → LUMO(48)
	$S_0 \to S_4$	320	0.1297	HOMO-3 → LUMO (27)
				HOMO-2 → LUMO (16)
	$S_0 \to S_6$	310	0.0106	HOMO-3 → LUMO (16)
				HOMO-2 → LUMO (31)
	$S_0 \to S_8$	303	0.0281	HOMO → LUMO+6 (33))
	$S_0 \to S_{14}$	286	0.0244	HOMO-7 → LUMO (25)
	$S_0 \to S_{15}$	284	0.0754	HOMO-6 → LUMO (25)
	$S_0 \to S_{16}$	283	0.0189	HOMO → LUMO(+4) (19)
				HOMO → LUMO+5 (20)
	$S_0 \to S_{17}$	282	0.0172	HOMO-3 → LUMO+2 (13)
	$S_0 \to S_{18}$	281	0.0159	HOMO-2 → LUMO+1 (23)
	$S_0 \to S_{19}$	280	0.0204	HOMO-8 → LUMO (15)

Table S11. TD-DFT first Singlet-Singlet Excitation Calculations for model system **3a**.

Model	exc.	λ_{calc} (nm)	f (s)	contributions
3a	$S_0 \to S_1$	319	0.0667	HOMO → LUMO (47)
	$S_0 \to S_2$	295	0.0182	HOMO-3 → LUMO(16)
				HOMO-1 → LUMO (29)
	$S_0 \to S_5$	284	0.0321	HOMO-4 → LUMO (16)
	$S_0 \to S_{12}$	259	0.0423	HOMO-6 → LUMO (13)
	$S_0 \to S_{13}$	258	0.1696	HOMO-6 → LUMO (24)
	$S_0 \to S_{14}$	257	0.0126	HOMO-2 → 109 (15)
	$S_0 \to S_{16}$	255	0.0127	HOMO-4 → LUMO+2 (21)
	$S_0 \to S_{19}$	250	0.0210	HOMO-4 → LUMO+2 (15)

Table S12. TD-DFT first Singlet-Singlet Excitation Calculations for model system **4a**.

Model	exc.	λ_{calc} (nm)	ƒ (s)	contributions
4a	$S_0 \rightarrow S_1$	357	0.0806	HOMO → LUMO (48)
	$S_0 \rightarrow S_2$	338	0.0841	HOMO → LUMO+1 (48)
	$S_0 \rightarrow S_4$	302	0.039	HOMO-2 → LUMO (22)
				HOMO-1 → LUMO+1 (19)
	$S_0 \rightarrow S_5$	300	0.0278	HOMO-3 → LUMO(37)
	$S_0 \rightarrow S_6$	296	0.0147	HOMO-2 → LUMO (24)
	$S_0 \rightarrow S_9$	290	0.0106	HOMO-6 → LUMO (18)
	$S_0 \rightarrow S_{13}$	282	0.0147	HOMO-2 → LUMO+1 (39)
	$S_0 \rightarrow S_{15}$	276	0.0185	HOMO-8 → LUMO (18)
				HOMO-3 → LUMO+1 (19)
	$S_0 \rightarrow S_{16}$	274	0.0272	HOMO-6 → LUMO+1 (29)

Table S13. Details of data collection and refinement for {[{Au(C$_6$Cl$_5$)$_2$}Tl(TACN)]$_2$}$_n$ (1).

Complex	1
Empirical formula	C$_{18}$H$_{15}$AuCl$_{10}$N$_3$Tl
Formula weight	1029.17
Temperature/K	105.24
Crystal system	Triclinic
Space group	P-1
a/Å	9.8906(14)
b/Å	10.6441(15)
c/Å	13.108(2)
α/°	86.361(5)
β/°	87.662(5)
γ/°	73.880(5)
Volume/Å^3	1322.7(3)
Z	2
ρ_{calc}g/cm^3	2.582
μ/mm^{-1}	12.649
F(000)	946.0
Crystal size/mm^3	0.607 × 0.143 × 0.098
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.048 to 55.788
Reflections collected	26098
Independent reflections	6265 [R$_{int}$ = 0.1112]
Data/restraints/parameters	6265/0/307
Goodness-of-fit on F^2	0.999
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0481, wR$_2$ = 0.1026
Final R indexes [all data]	R$_1$ = 0.0907, wR$_2$ = 0.1201
Largest diff. peak/hole / e Å^{-3}	3.46/-1.97

Table S14. Details of data collection and refinement for [{Au(C$_6$Cl$_5$)$_2$}Ag(TACN)] (3).

Complex	3
Empirical formula	C$_{18}$H$_{15}$AgAuCl$_{10}$N$_3$
Formula weight	932.67
Temperature/K	109.99
Crystal system	Triclinic
Space group	P-1
a/Å	8.9202(7)
b/Å	11.8246(8)
c/Å	13.9123(11)
α/°	107.085(2)
β/°	100.045(3)
γ/°	106.406(2)
Volume/Å^3	1291.47(17)
Z	2
ρ_{calc}g/cm^3	2.398
μ/mm^{-1}	7.482
F(000)	880.0
Crystal size/mm^3	0.383 × 0.104 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.004 to 55.84
Reflections collected	26368
Independent reflections	6159 [R$_{int}$ = 0.0575]
Data/restraints/parameters	6159/0/299
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0308, wR$_2$ = 0.0632
Final R indexes [all data]	R$_1$ = 0.0441, wR$_2$ = 0.0682
Largest diff. peak/hole / e Å^{-3}	1.63/-1.77

Table S15. Details of data collection and refinement for

[{Au(C₆F₅)₂}{Ag(TACN)}₂Au(C₆F₅)₂] (4).

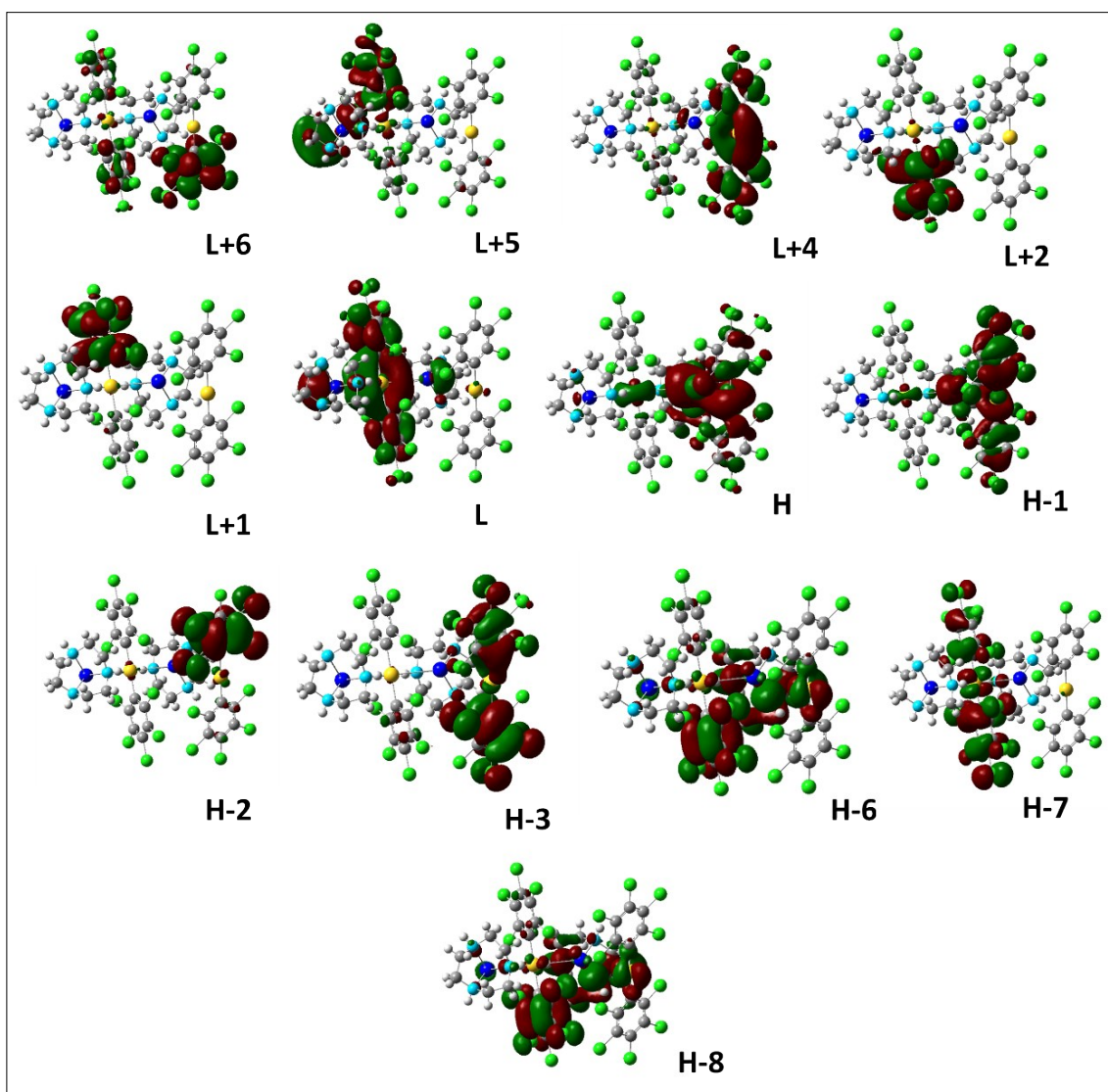| Compound	4
Empirical formula	$C_{18}H_{15}AgAuF_{10}N_3$
Formula weight	768.17
Temperature/K	101.05
Crystal system	Monoclinic
Space group	C2/c
a/Å	23.744(3)
b/Å	8.6609(10)
c/Å	20.843(3)
α/°	90
β/°	109.049(5)
γ/°	90
Volume/Å³	4051.5(10)
Z	8
ρ_{calc}g/cm³	2.519
μ/mm⁻¹	8.303
F(000)	2880.0
Crystal size/mm³	0.709 × 0.107 × 0.061
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.67 to 53.02
Reflections collected	27708
Independent reflections	4143 [R_{int} = 0.2373]
Data/restraints/parameters	4143/301/299
Goodness-of-fit on F²	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0576, wR_2 = 0.0705
Final R indexes [all data]	R_1 = 0.1195, wR_2 = 0.0826
Largest diff. peak/hole / e Å⁻³	1.18/-1.19

Figure S1. Most important frontier molecular orbitals (isovalue = 0.02) for model system **1a** (L=LUMO; H=HOMO).
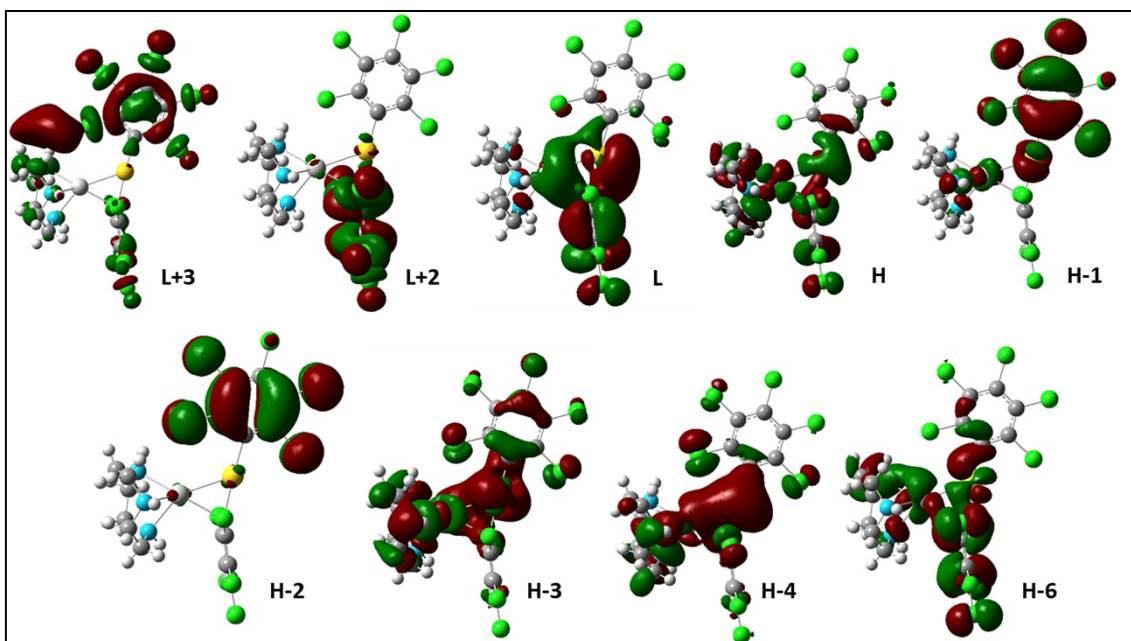
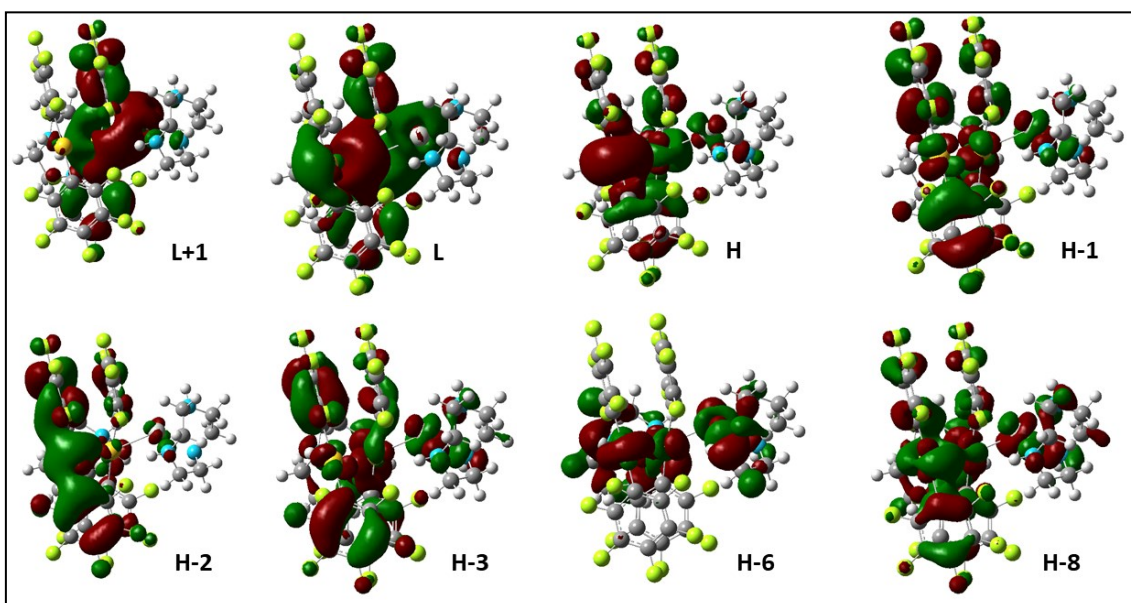**Figure S2.** Most important frontier molecular orbitals (isovalue = 0.02) for model system **3a** (L=LUMO; H=HOMO).

Figure S3. Most important frontier molecular orbitals (isovalue = 0.02) for model system **4a** (L=LUMO; H=HOMO).