Influence of the number of metallophilic interactions and structures on the optical properties of heterometallic Au/Ag complexes with mixed-donor macrocyclic ligands.

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Supporting Information

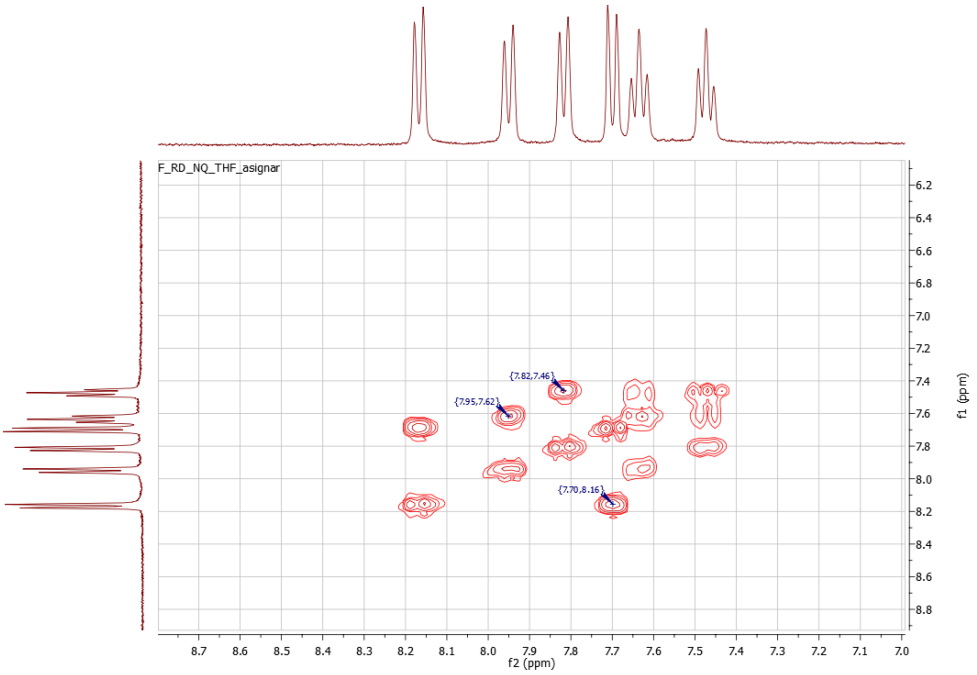

Figure S1: COSY of free ligand L_3 in THF-D_8 solution.

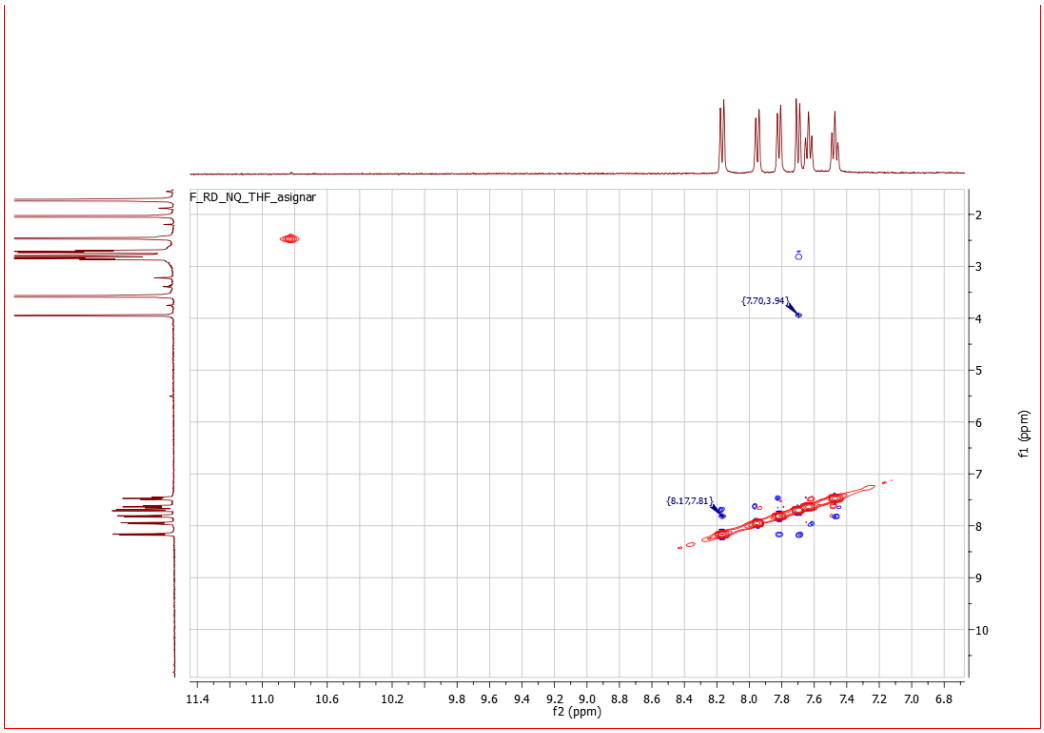

Figure S2: NOESY of free ligand L_3 in THF-D_8 solution.

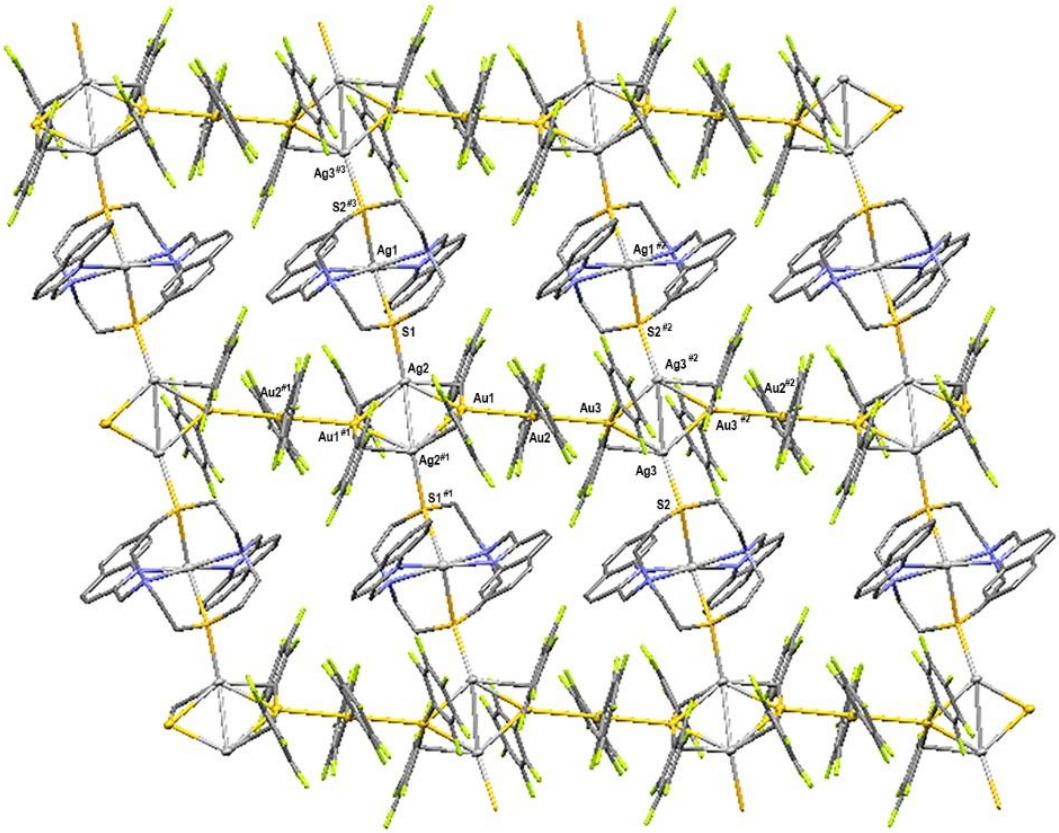

Figure S3. Polymeric 2-D crystal structure of **6**.

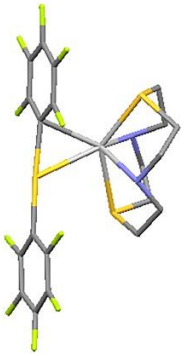

Figure S4. Molecular structure of **1**.

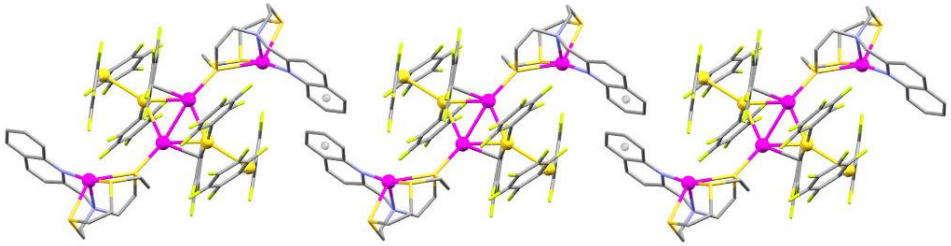

Figure S5. Extended **1-D** polymeric crystal structure of **5**·2THF.

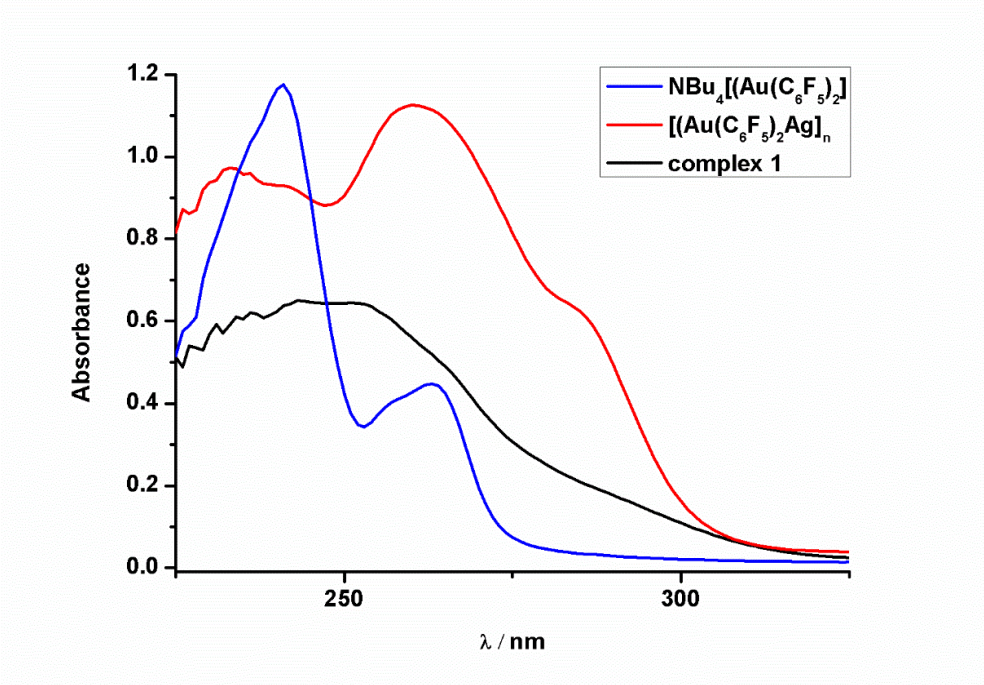

Figure S6. UV-vis spectra in THF solution 5x10^{-4} M of **1**.

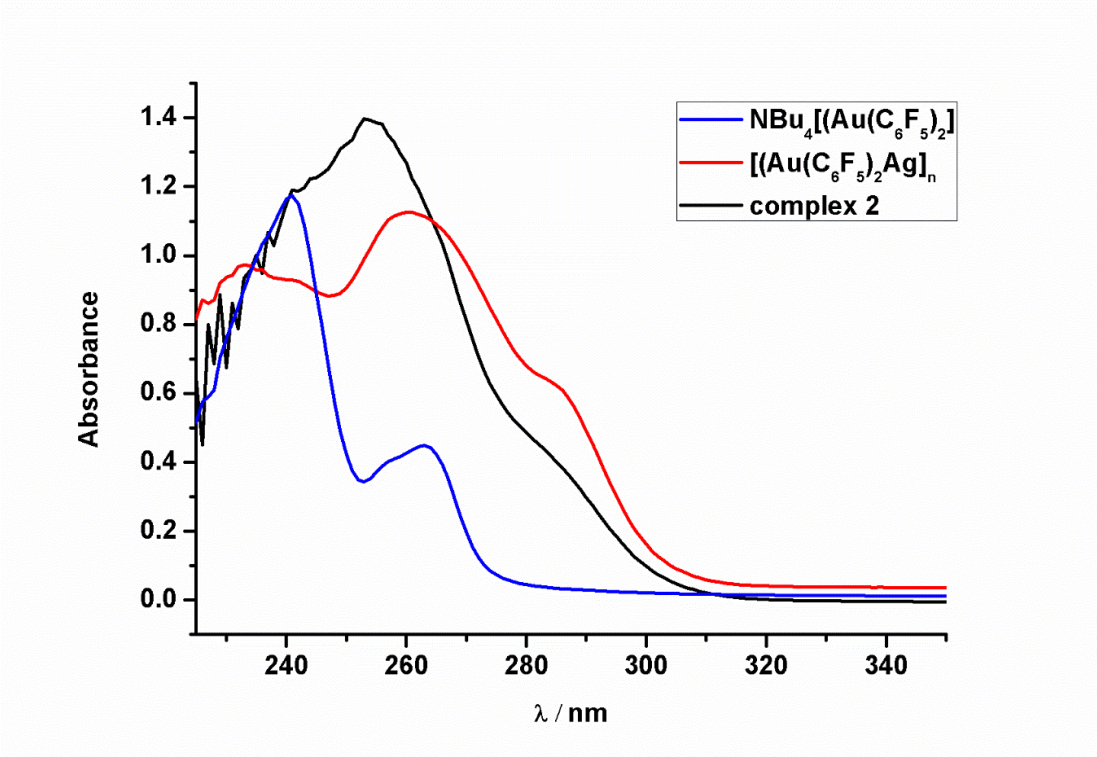

Figure S7. UV-vis spectra in THF solution 5x10^{-4} M of **2**.

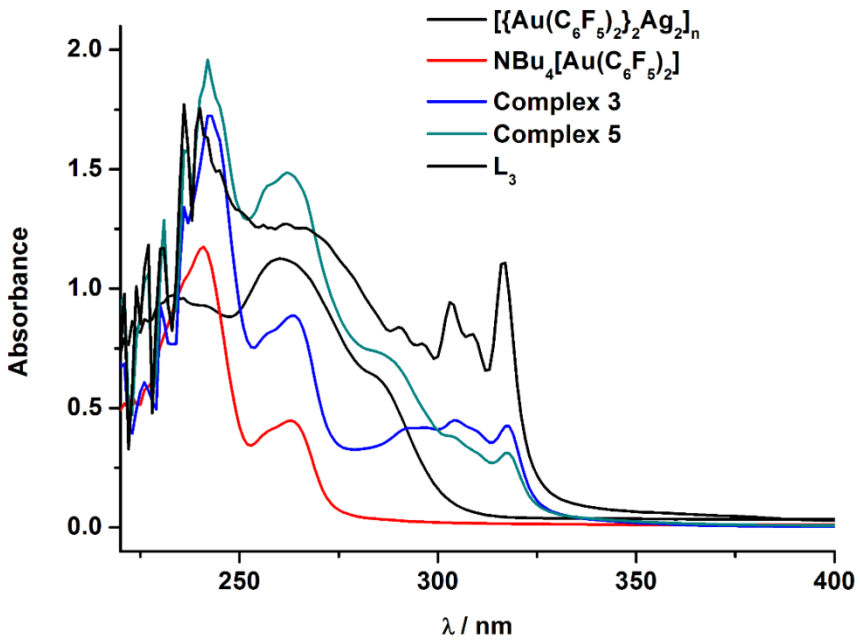

Figure S8. UV-vis spectra in THF solution 5x10^{-4} M of **3** and **5**.

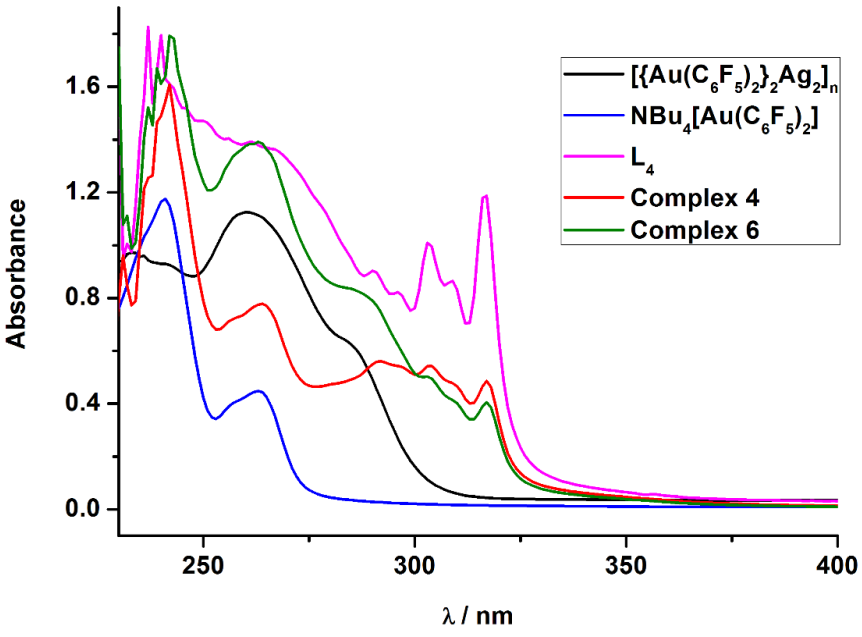

Figure S9. UV-vis spectra in THF solution 5x10^{-4} M of **4** and **6**.

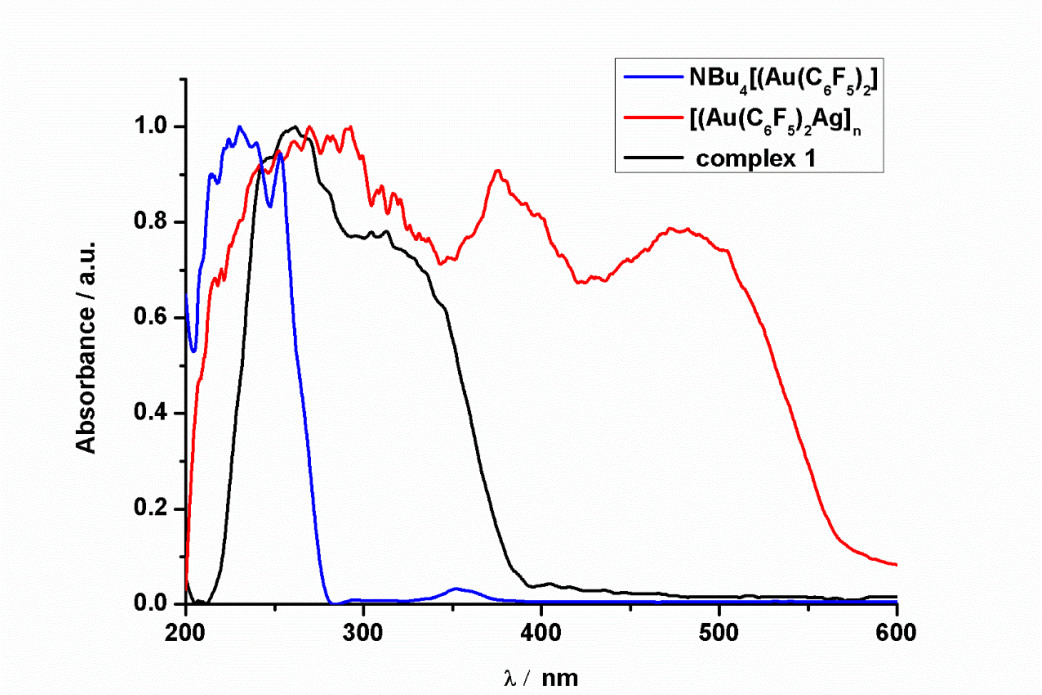

Figure S10. UV-vis spectra in solid state of **1**.

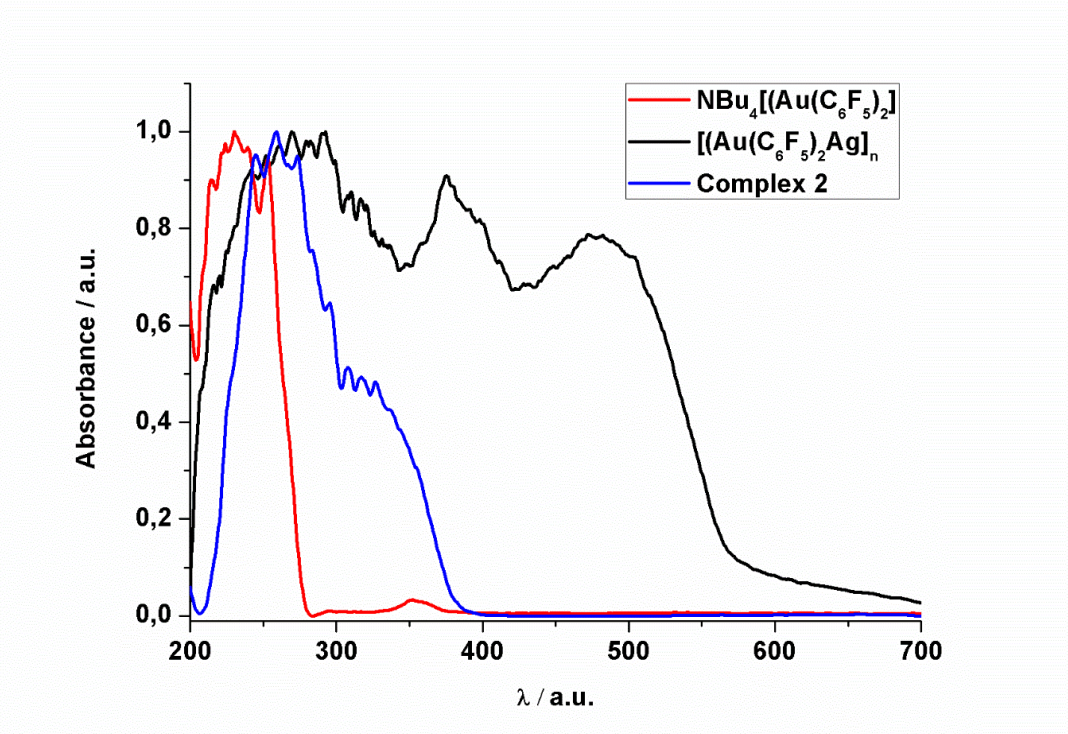

Figure S11. UV-vis spectra in solid state of **2**.

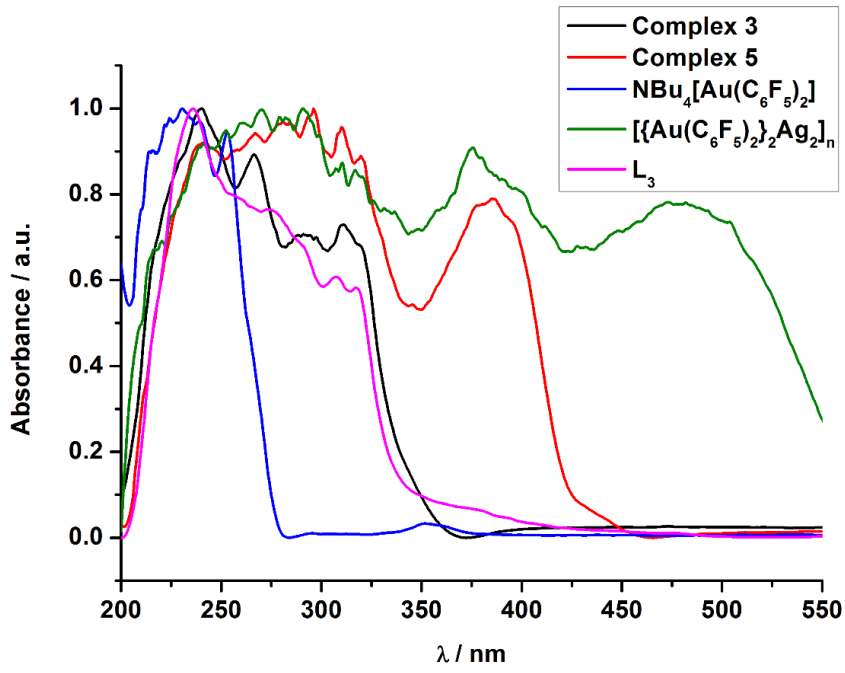

Figure S12. UV-vis spectra in solid state of **3** and **5**.

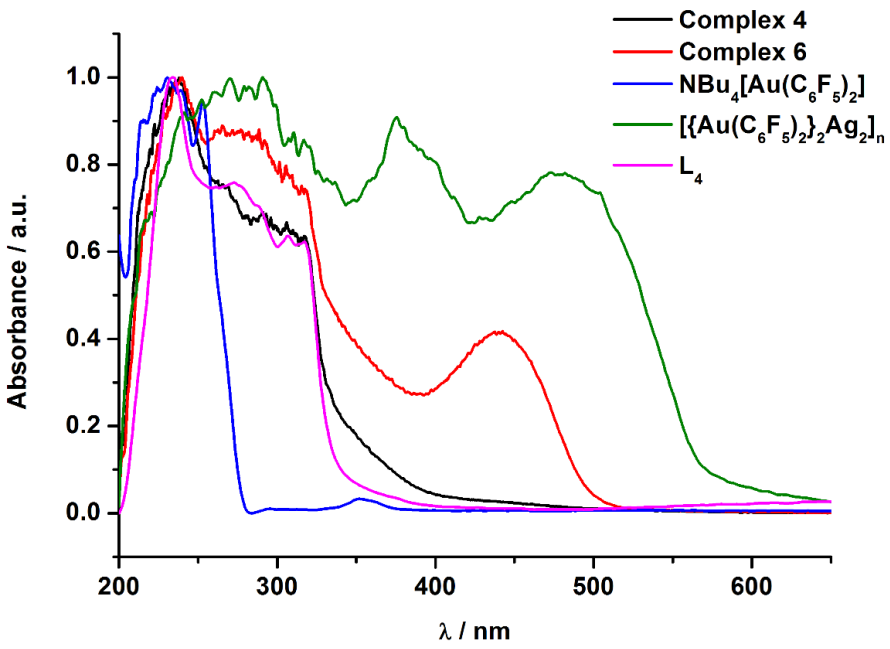

Figure S13. UV-vis spectra in solid state of **4** and **6**.

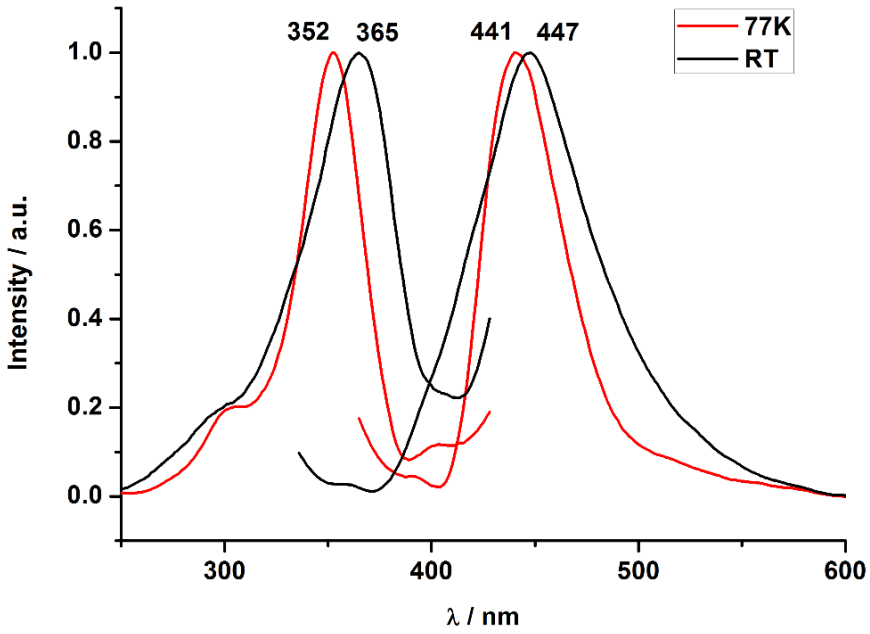

Figure S14. Luminescence in solid state of **1.**

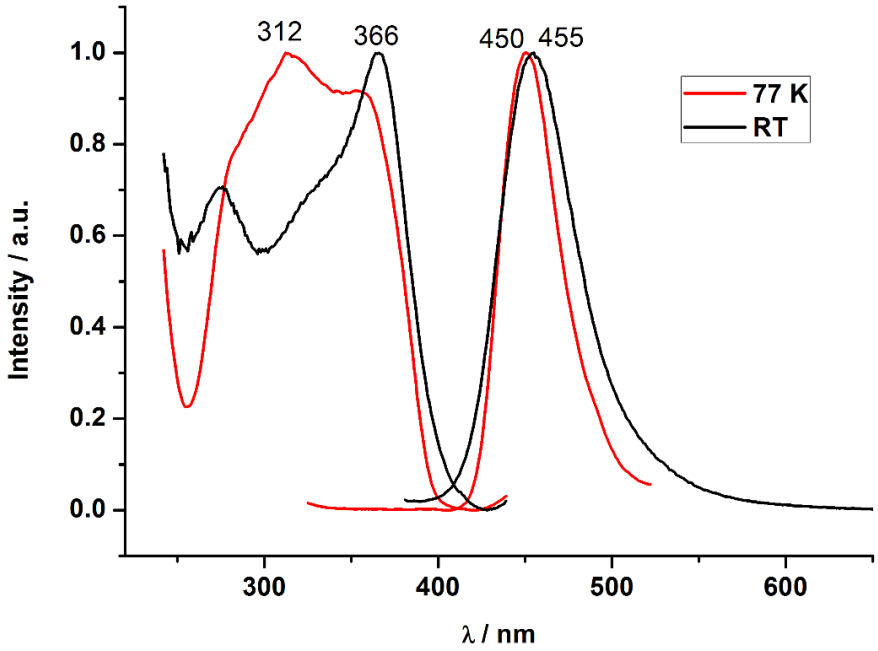

Figure S15. Luminescence in solid state of **2.**

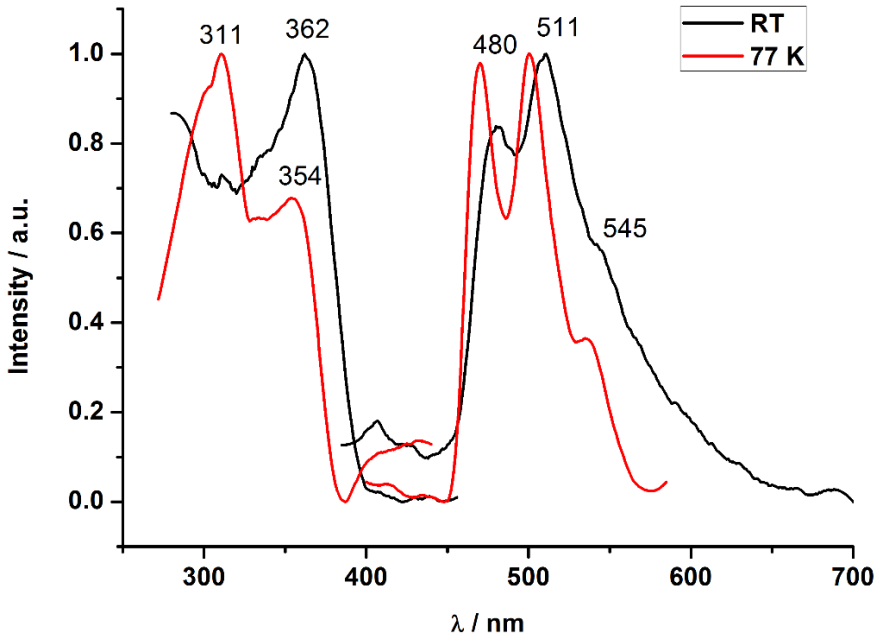

Figure S16. Luminescence in solid state of **3.**

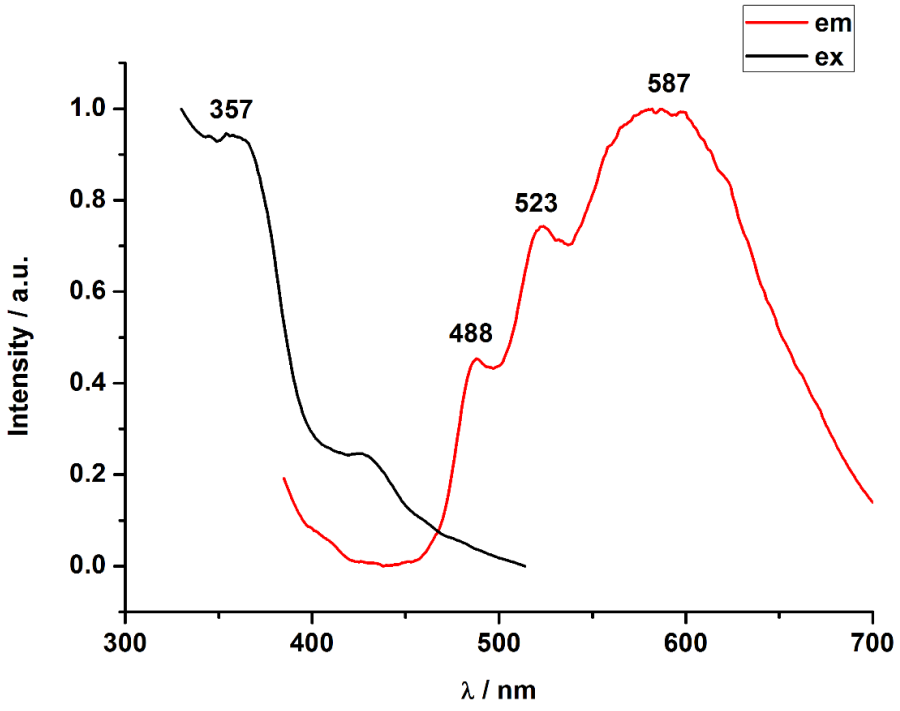

Figure S17. Luminescence in solid state of **4** at 77K.

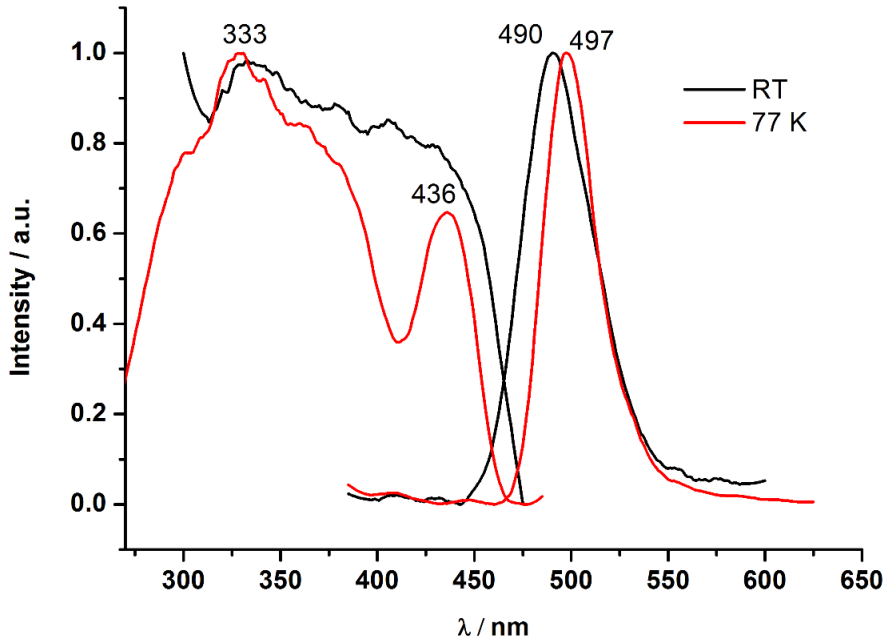

Figure S18. Luminescence in solid state of **5.**

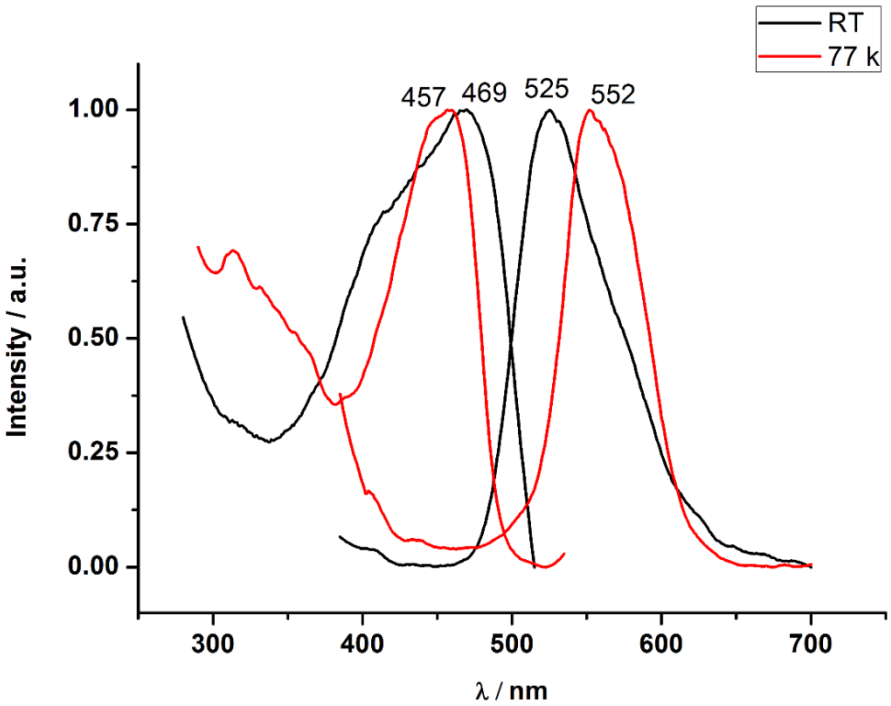

Figure S19. Luminescence in solid state of **6.**

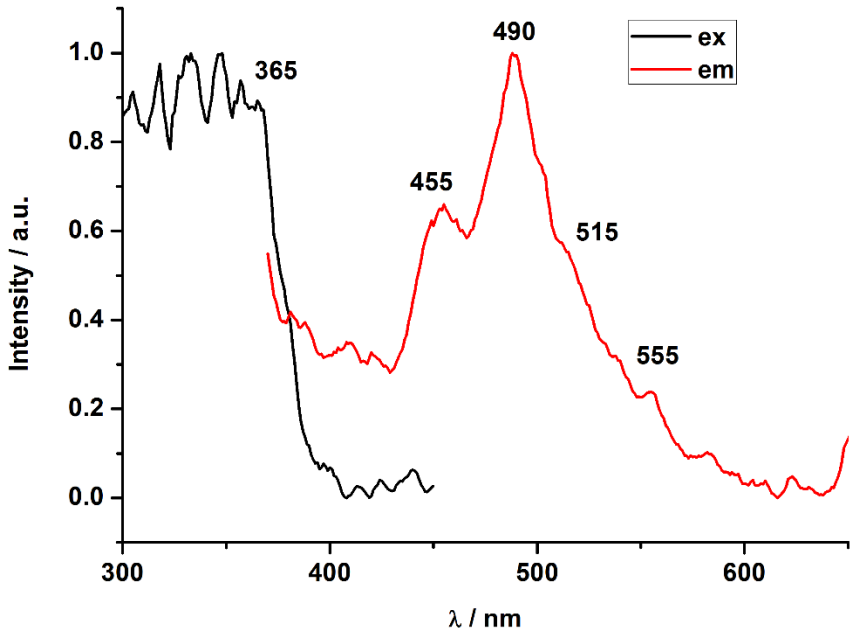

Figure S20. Luminescence in solid state of [Ag**L**$_3$]ClO$_4$ at RT.

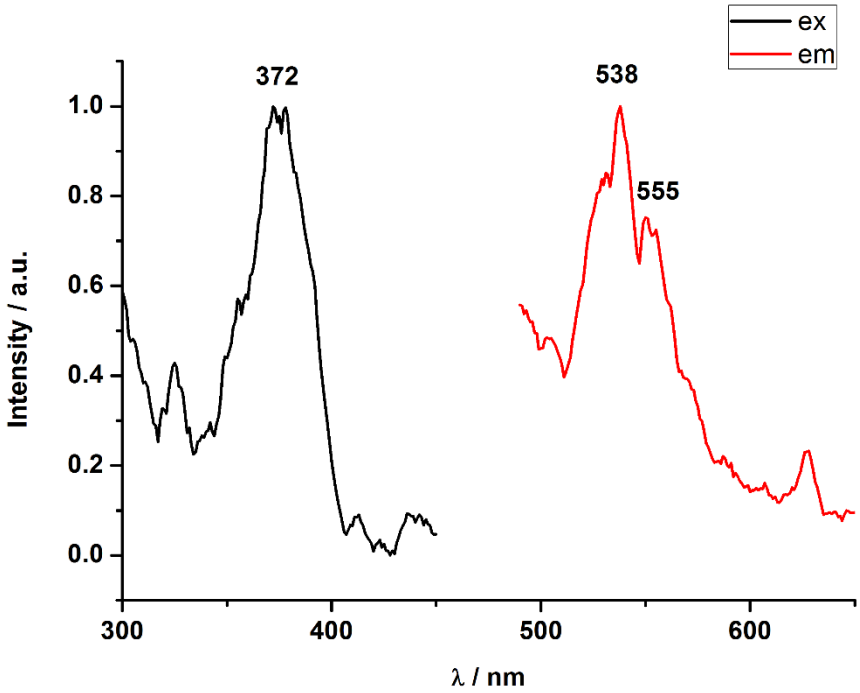

Figure S21. Luminescence in solid state of [Ag**L**$_4$]ClO$_4$ at RT.

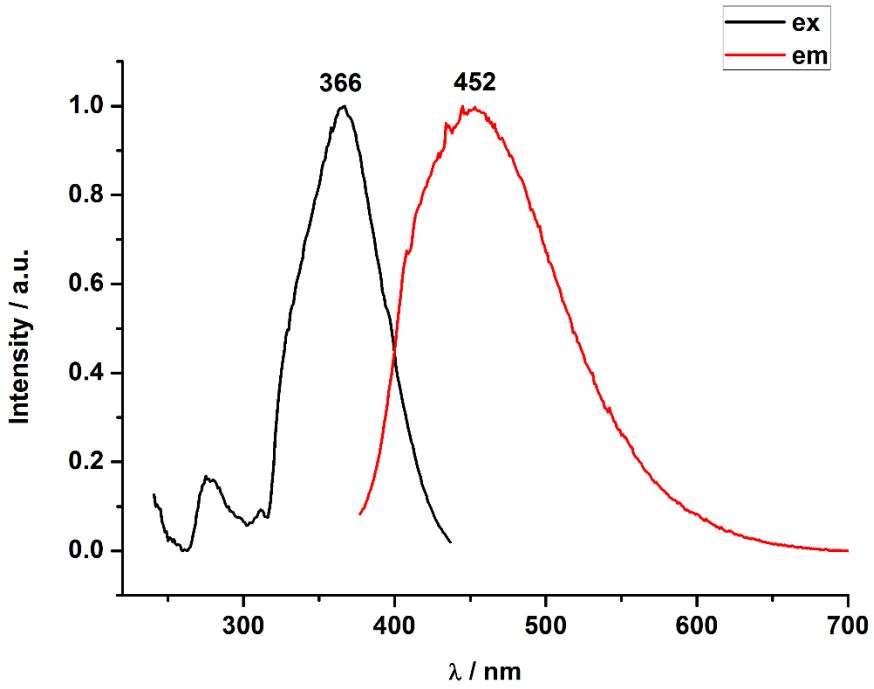

Figure S22. Luminescence in THF solution $5x10^{-4}$ M of **3** at RT.

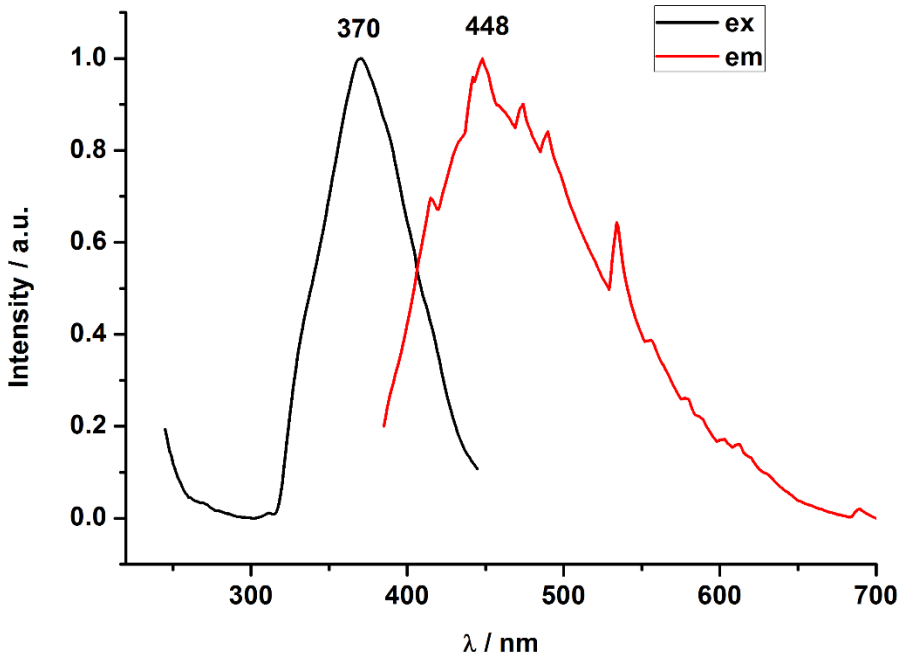

Figure S23. Luminescence in THF solution $5x10^{-4}$ M of **4** at RT.

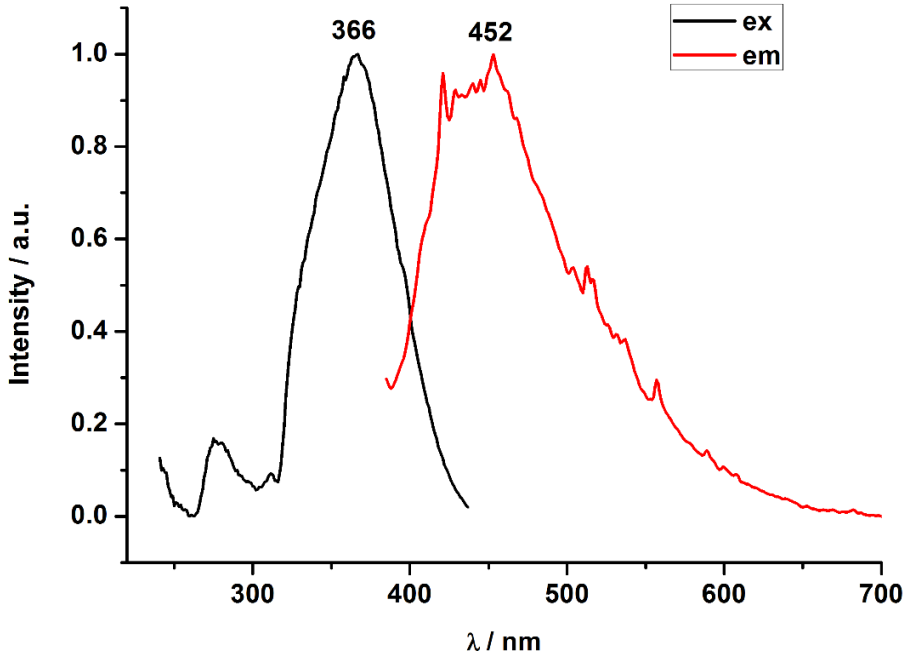

Figure S24. Luminescence in THF solution $5x10^{-4}$ M of **5** at RT.

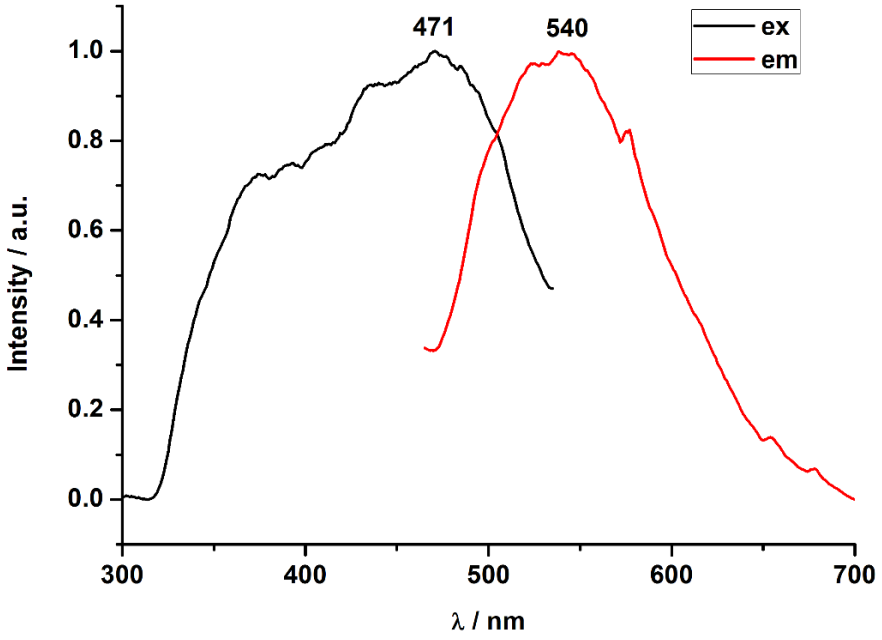

Figure S25. Luminescence in THF solution $5x10^{-4}$ M of **6** at RT.

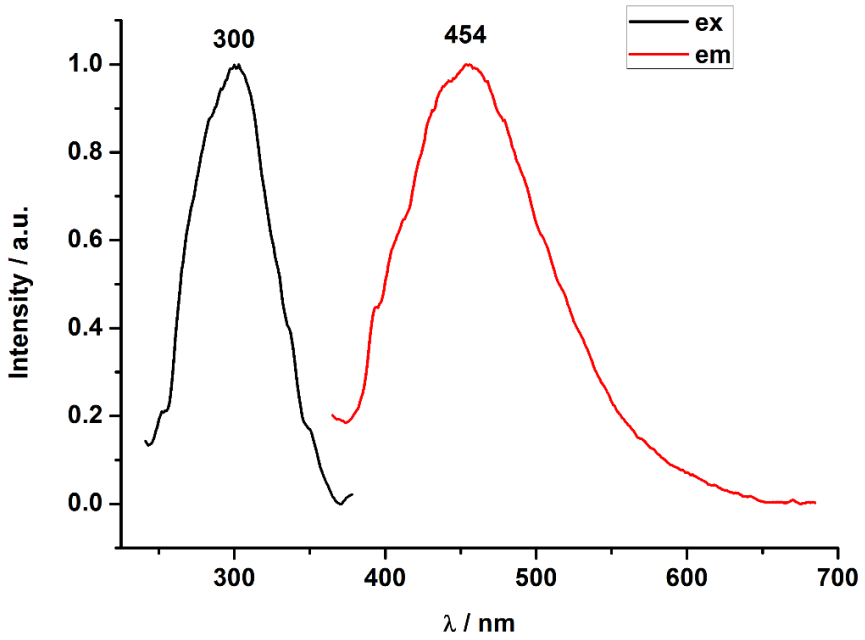

Figure S26. Luminescence in THF solution $5x10^{-4}$ M of Complex [Ag**L**$_3$]ClO_4 at RT.

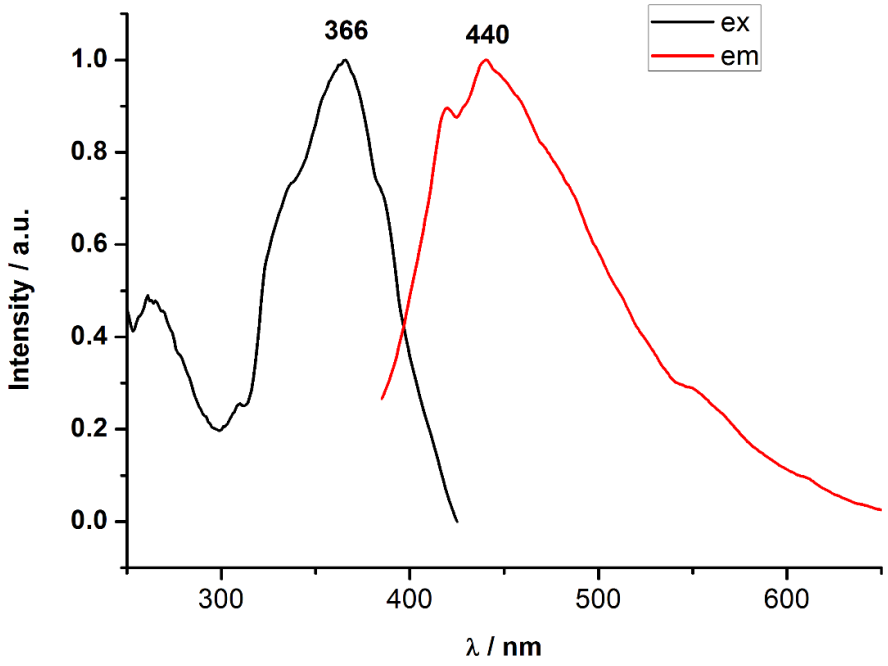

Figure S27. Luminescence in THF solution $5x10^{-4}$ M of [Ag**L**$_4$]ClO_4 at RT.

Table S1. Selected bond lengths [Å] and angles [°] for **6**.

Au(1)-Au(2)	3.0617(13)
Au(2)-Au(3)	3.0995(13)
Au(1)-Ag(2)	2.7220(19)
Au(1)-Ag(2)#1	2.759(2)
Au(3)-Ag(3)	2.728(2)
Au(3)-Ag(3)#2	2.725(2)
Ag(2)-Ag(2)#1	3.081(3)
Ag(3)-Ag(3)#2	3.113(3)
Au(1)-Au(2)-Au(3)	179.32(5)

Symmetry transformations used to generate equivalent atoms:

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

Table S2. Population Analysis (%) for Model Systems **1a** and **2a**.

Model	Orbital	Au	Ag	C_6F_5	Ligand
1a	LUMO+5	13	35	30	22
	LUMO+4	31	37	20	13
	LUMO+3	12	70	2	16
	LUMO+2	30	35	27	8
	LUMO+1	1	41	19	38
	LUMO	5	28	32	35
	HOMO	8	20	2	70
	HOMO-1	16	14	31	39
	HOMO-2	23	7	44	26
	HOMO-3	11	5	18	67
	HOMO-4	16	17	40	27
2a	LUMO+4	52	30	2	9
	LUMO+3	38	16	4	25
	LUMO	34	23	33	6
	HOMO	51	19	18	10
	HOMO-2	6	27	3	43
	HOMO-3	7	26	3	39
	HOMO-4	33	4	61	1
	HOMO-8	3	3	91	1
	HOMO-10	25	13	55	3

Table S3. Population Analysis (%) for Model Systems **5a**. $_T$ symbolizes the parts of the molecule that form the tetramer.

Model	Orbital	Ag	Ligand	$C_6F_{5\_T}$	$Au_{\_T}$	$Ag_{\_T}$
5a	LUMO+15	21	38	17	5	19
	LUMO+13	1	94	2	1	2
	LUMO+9	55	6	9	22	8
	LUMO+5	14	26	10	22	29
	LUMO+2	1	35	1	52	10
	LUMO+1	1	0	99	0	0
	LUMO	1	0	99	0	0
	HOMO	0	27	0	67	6
	HOMO-2	0	85	0	15	0
	HOMO-3	0	30	1	68	2
	HOMO-6	11	65	23	1	1
	HOMO-8	24	18	54	1	3
	HOMO-9	20	30	46	1	3
	HOMO-10	1	88	2	9	0
	HOMO-15	9	54	21	6	10
	HOMO-17	7	24	16	48	6
	HOMO-18	1	87	3	9	1
	HOMO-19	10	30	22	35	3
	HOMO-20	7	75	14	3	1
	HOMO-27	2	1	91	6	0
	HOMO-28	2	2	87	7	2
	HOMO-31	0	0	99	0	0
	HOMO-32	0	0	99	0	0

Table S4. Population Analysis (%) for Model Systems **6a** and **6b.** $_T$ symbolizes the parts of the molecule that form the tetramer. $_L$ refers to the Ag(I) center that is totally coordinated to the macrocyclic ligand.

Model		C_6F_5	Au	$C_6F_{5\_T}$	Ag_T	Au_T
6a	LUMO+3	1	3	28	38	30
	LUMO+2	0	1	15	54	30
	LUMO+1	0	1	16	52	31
	LUMO	2	5	28	17	49
	HOMO	51	19	18	5	7
	HOMO-1	38	20	18	8	16
	HOMO-2	74	3	18	1	3
		C_6F_5	Au	Ag_L	Ag_T	L_4
6b	LUMO+1	26	41	0	33	0
	LUMO	28	41	0	32	0
	HOMO-1	72	6	1	3	18
	HOMO-2	35	4	15	4	43
	HOMO-3	22	2	13	3	60
	HOMO-4	76	8	2	4	10
	HOMO-5	91	5	0	2	2
	HOMO-6	60	5	1	4	30
	HOMO-8	53	5	1	3	38

Table **S5.** TD-DFT First Singlet−Singlet Excitation Calculations for Model Systems **1a** and **2a**, and Lowest Singlet−Triplet Excitations for Model **2a**.

Model	exc.[a]	λ_{calc} (nm)	f (s)[b]	contributions[c]
1a	$S_0 \rightarrow S_1$	345.5	0.0186	HOMO →LUMO (61.3)
				HOMO →LUMO(+1)(34.6)
	$S_0 \rightarrow S_2$	320.7	0.0220	HOMO →LUMO (31.3)
				HOMO →LUMO(+1)(55.1)
	$S_0 \rightarrow S_3$	316.0	0.0115	HOMO(-1) →LUMO (57.5)
	$S_0 \rightarrow S_4$	301.2	0.0673	HOMO(-1) →LUMO (17.3)
				HOMO-1 →LUMO(+1)(63.5)
	$S_0 \rightarrow S_5$	285.1	0.0415	HOMO(-3) →LUMO (18.3)
				HOMO(-2) →LUMO (25.3)
	$S_0 \rightarrow S_6$	284.3	0.0604	HOMO(-2) →LUMO (36.0)
				HOMO(-1) →LUMO(+2)(20.1)
				HOMO →LUMO(+2)(30.6)
	$S_0 \rightarrow S_7$	283.2	0.0171	HOMO(-3) →LUMO (19.9)
				HOMO(-2) →LUMO (15.7)
				HOMO →LUMO(+2)(39.4)
	$S_0 \rightarrow S_8$	278.3	0.0147	HOMO(-1) →LUMO(+2)(48.2)
	$S_0 \rightarrow S_9$	272.0	0.0634	HOMO(-2) →LUMO(+1)(66.2)
	$S_0 \rightarrow S_{10}$	265.1	0.0350	HOMO(-4) →LUMO (37.1)
	$S_0 \rightarrow S_{11}$	262.5	0.0110	HOMO(-4) →LUMO (17.3)
				HOMO(-3) →LUMO(+1)(32.1)
	$S_0 \rightarrow S_{12}$	261.3	0.0173	HOMO →LUMO(+3)(61.3)
	$S_0 \rightarrow S_{13}$	251.3	0.0227	HOMO →LUMO(+4)(18.0)
	$S_0 \rightarrow S_{14}$	248.0	0.0258	HOMO →LUMO(+5)(79.2)
2a	$S_0 \rightarrow S_1$	333.2	0.5308	HOMO → LUMO (98.0)
	$S_0 \rightarrow S_2$	281.8	0.2658	HOMO(-4) → LUMO (97.1)
	$S_0 \rightarrow S_3$	257.2	0.0241	HOMO(-8) → LUMO (85.9)
	$S_0 \rightarrow S_4$	252.8	0.0351	HOMO(-10) → LUMO (46.0)
	$S_0 \rightarrow S_5$	251.3	0.0118	HOMO(-10) → LUMO (30.6)
				HOMO(-3) → LUMO(+3) (16.5)
				HOMO(-2) → LUMO(+4) (15.41)
	$S_0 \rightarrow T_1$	392.0	0.0000	HOMO → LUMO (63.8)

[a]Only excitations with larger oscillator strengths are included among the first 10 singlet excitation calculations. [b]Oscillator strength (f) shows the mixed representation of both velocity and length representations. [c]Value is $2 \times |\text{coeff}|^2 \times 100$

Table **S6.** TD-DFT First Singlet−Singlet Excitation Calculations for Model Systems **5a**, **6a** and **6b**.

Model	exc.[a]	λ_{calc} (nm)	f (s)[b]	contributions[c]
5a	$S_0 \rightarrow S_3$	391	0.6549	HOMO→LUMO+2 (100%)
	$S_0 \rightarrow S_{13}$	342	0.0415	HOMO-2→LUMO+2 (100%)
	$S_0 \rightarrow S_{43}$	299	0.0391	HOMO-10→LUMO+2 (15%)
				HOMO-9→LUMO+2 (47%)
				HOMO-8→LUMO+2 (21%)
	$S_0 \rightarrow S_{47}$	296	0.0105	HOMO→LUMO+7 (82%)
	$S_0 \rightarrow S_{48}$	294	0.0237	HOMO-10→LUMO+2 (63%)
				HOMO-6→LUMO+2 (13%)
	$S_0 \rightarrow S_{58}$	285	0.0354	HOMO-32→LUMO (10%)
				HOMO-28→LUMO (23%)
				HOMO-27→LUMO (26%)
	$S_0 \rightarrow S_{59}$	284	0.0172	HOMO-31→LUMO+1 (10%)
				HOMO-28→LUMO+1 (27%)
				HOMO-27→LUMO+1 (23%)
	$S_0 \rightarrow S_{60}$	283	0.0318	HOMO-20→LUMO (10%)
				HOMO-18→LUMO (10%)
				HOMO-3→LUMO+5 (15%)
				HOMO→LUMO+9 (15%)
				HOMO→LUMO+15 (16%)
	$S_0 \rightarrow S_{67}$	279	0.0111	HOMO→LUMO+13 (82%)
	$S_0 \rightarrow S_{69}$	278	0.0750	HOMO-17→LUMO+2 (23%)
				HOMO-15→LUMO+2 (47%)
	$S_0 \rightarrow S_{70}$	277	0.0118	HOMO-19→LUMO+2 (10%)
				HOMO-17→LUMO+2 (27%)
				HOMO-15→LUMO+2 (23%)
6a	$S_0 \rightarrow S_1$	504.1	0.1148	HOMO→LUMO (93%)
	$S_0 \rightarrow S_2$	484.8	0.5438	HOMO-1→LUMO(92%)
	$S_0 \rightarrow S_3$	476.0	0.0307	HOMO-1→LUMO+1(21%)
				HOMO→LUMO+1(72%)
	$S_0 \rightarrow S_4$	456.0	0.0345	HOMO-2→LUMO(45%)
				HOMO-1→LUMO+1(39%)
	$S_0 \rightarrow S_6$	446.6	0.0108	HOMO-2→LUMO(21%)
				HOMO-1→LUMO+2(72%)
				HOMO→LUMO+2(21%)
6b	$S_0 \rightarrow S_2$	377.9	0.0208	HOMO-1→LUMO (87%)
	$S_0 \rightarrow S_4$	362.4	0.0798	HOMO-6→LUMO(24%)
				HOMO-2→LUMO(53%)
	$S_0 \rightarrow S_5$	359.8	0.0671	HOMO-5→LUMO(58%)
				HOMO-4→LUMO(30%)
	$S_0 \rightarrow S_6$	355.7	0.0160	HOMO-6→LUMO+1(14%)
				HOMO-5→LUMO+1(32%)
				HOMO-4→LUMO+1(38%)
				HOMO-3→LUMO+1(12%)
	$S_0 \rightarrow S_7$	343.2	0.0495	HOMO-8→LUMO+1(13%)
				HOMO-3→LUMO+1(41%)
				HOMO-2→LUMO+1(25%)

[a]Only excitations with larger oscillator strengths are included among the first 10 singlet excitation calculations. [b]Oscillator strength (*f*) shows the mixed representation of both velocity and length representations. [c]Value is $2 \times |\text{coeff}|^2 \times 100$