New Journal of Chemistry

Electronic Supplementary Information

Structural and electronic impact on the photophysical and biological properties of a series of Cu^{I} and Ag^{I} complexes with triphenylphosphine and pyrimidine-type thiones.

Panagiotis A. Papanikolaou,*[a] Anastasios G. Papadopoulos,*[b] Eleni G. Andreadou,[c] Antonios Hatzidimitriou,[a] Philip J. Cox,[d] Anastasia A. Pantazaki[c] and Paraskevas Aslanidis*[a]

[a] Aristotle University of Thessaloniki, Department of Chemistry, Laboratory of Inorganic Chemistry, P.O.B. 135, GR-541 24 Thessaloniki, Greece. Fax: +30 2310 997738; E-mail: panpapan@chem.auth.gr, hatzidim@chem.auth.gr, aslanidi@chem.auth.gr

[b] Aristotle University of Thessaloniki, Department of Chemistry, Laboratory of Applied Quantum Chemistry, P.O.B. 135, GR-541 24 Thessaloniki, Greece. Fax: +30 2310 997738; E-mail: anastp@chem.auth.gr

[c] Aristotle University of Thessaloniki, Department of Chemistry, Laboratory of Biochemistry, P.O.B. 135, GR-541 24 Thessaloniki, Greece; E-mail: natasa@chem.auth.gr

[d] School of Pharmacy, The Robert Gordon University, Schoolhill, Aberdeen AB10 1FR, Scotland, United Kingdom. Email: p.j.cox@rgu.ac.uk

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Table S1 Crystallographic details for the isolated Cu^{I} and Ag^{I} complexes.

Compound	**1.$CHCl_3$**	**2.CH_3OH**	**3.CH_3OH**	**4.CH_3OH**	**5.CH_3OH**	**6.CH_3OH**
Formula	$C_{45}H_{39}B_1Cl_3Cu_1F_4N_4P_2S_2$	$C_{59}H_{53}B_1Cu_1F_4N_2O_1P_3S_1$	$C_{49}H_{50}B_1Cu_1F_4N_4O_1P_2S_2$	$C_{61}H_{57}B_1Cu_1F_4N_2O_1P_3S_1$	$C_{59}H_{53}Ag_1N_3O_4P_3S_1$	$C_{61}H_{57}Ag_1N_3O_4P_3S_1$
Formula weight	1018.62	1081.42	987.34	1109.47	1100.94	1129.00
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Temperature	295 K	295 K	100(2) K	295 K	295 K	295 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 13.1382(8) Å *b* = 14.4016(9) Å *c* = 14.7271(13) Å *α* = 118.761(3)° *β* = 102.731(5)° *γ* = 91.598(4)°	a = 12.5375(5) Å *b* = 13.8679(5) Å *c* = 16.2676(6) Å *α* = 91.247(2)° *β* = 108.579(2)° *γ* = 90.431(2)°	a = 11.8722(8) Å *b* = 14.4982(10) Å *c* = 15.3775(11) Å *α* = 69.538(3)° *β*= 75.633(3)° *γ* = 85.560(4)°	a = 12.7182(5) Å *b* = 14.0670(6) Å *c* = 16.3036(6) Å *α* = 91.436(2)° *β*= 110.236(2)° *γ* = 90.267(2)°	a = 12.6902(6) Å *b* = 13.9321(6) Å *c* = 16.2986(8) Å *α* = 90.674(3)° *β*= 109.412(3)° *γ* = 91.674(2)°	a = 12.7507(4) Å *b* = 14.0470(5) Å *c* = 16.5484(6) Å *α* = 91.487(2)° *β*= 111.143(2)° *γ* = 92.621(2)°
Volume	2353.3(3) $Å^3$	2680.10(18) $Å^3$	2402.4(3) $Å^3$	2735.65(19) $Å^3$	2715.9(2) $Å^3$	2758.68(17) $Å^3$
Z	2	2	2	2	2	2
Absorption coefficient (μ)	0.843 mm^{-1}	0.592 mm^{-1}	0.665 mm^{-1}	0.582 mm^{-1}	0.547 mm^{-1}	0.540 mm^{-1}
Density (calculated)	1.43743 Mg/m^3	1.340 Mg/m^3	1.365 Mg/m^3	1.347 Mg/m^3	1.346 Mg/m^3	1.359 Mg/m^3
Crystal size	0.19 × 0.25 × 0.42 mm	0.31 × 0.34 × 0.42 mm	0.16 x 0.14 x 0.06 mm	0.31 x 0.36 x 0.40 mm	0.23× 0.26 × 0.34 mm	0.32 × 0.33 × 0.45 mm
Theta range for data collection	1.608 to 26.911°	1.714 to 30.655°	2.332 to 27.520°	1.332 to 28.903°	1.325 to 33.323°	1.321 to 29.798°
F(000)	1040	1120	1024	1152	1136	1168
Reflections collected	67144	54104	32418	48373	100427	75227
Independent reflections	10182 [R(int) = 0.044]	16311[R(int) = 0.050]	10986 [R(int) = 0.0519]	14219 [R(int) = 0.047]	20603[R(int) = 0.042]	14469 [R(int) = 0.030]
Completeness up to theta	100.0% (theta=26.911°)	99.4% (theta=25.137°)	99.8% (theta=25.242°)	99.6% (theta=28.036°)	98.4% (theta=32.323°)	98.7% (theta=25.030°)
Data/restraints/parameters	5762/0/555	8508/0/645	10986/0/583	7702/19/663	9123/0/637	8754/0/658
Goodness-of-fit on F^2	1.0474	0.9985	1.061	1.0661	1.000	0.9991
Final R indices [I>2σ(I)]	R_1=0.0601, wR_1=0.0967	R_1=0.0647, wR_1=0.1154	R_1=0.0437, wR_1=0.1177	R_1=0.0546, wR_1=0.1073	R_1=0.0383, wR_1=0.0721	R_1=0.0523, wR_1=0.0970
R indices (all data)	R_2=0.1468, wR_2=0.2104	R_2=0.1117, wR_2=0.1323	R_2=0.0503, wR_2=0.1227	R_2=0.0981, wR_2=0.1235	R_2=0.0770, wR_2=0.0952	R_2=0.0987, wR_2=0.1148
Final weighting scheme	$w= w' \times [1 - (\Delta F_{obs} / 6 \times \Delta F_{est})^2]^2$ $w'=[P_0T_0'(x) + P_1T_1'(x) + ...P_{n-1}T_{n-1}'(x)]^{-1}$ where $x=F_{calc}^2/F_{calc}^2{}_{max}$ and P_0 - P_{n-1} =1.25, 1.25, 0.181	$w=(1/4F_{obs}^2) \times 1$	$w=1/[\sigma^2(Fo^2)+(0.0695P)^2+1.28P]$ where $P=(Max(Fo^2,0) +2*Fc^2)/3$	$w= w' \times [1 - (\Delta F_{obs} / 6 \times \Delta F_{est})^2]^2$ $w'=[P_0T_0'(x) + P_1T_1'(x) + ...P_{n-1}T_{n-1}'(x)]^{-1}$ where $x=F_{calc}^2/F_{calc}^2{}_{max}$ and P_0 - P_{n-1} =3.08, 3.73, 1.26	$w=(1/4F_{obs}^2) \times 1$	$w=(1/4F_{obs}^2) \times 1$
Largest diff. peak and hole	0.63, – 0.41 e.$Å^{-3}$	0.82, – 0.62 e.$Å^{-3}$	1.135, – 0.527 e.$Å^{-3}$	0.86, – 0.72 e.$Å^{-3}$	1.27, – 0.51 e.$Å^{-3}$	1.51, – 0.61 e.$Å^{-3}$

Table S2 Energetic and geometrical parameters in the selected media and visualization of the two tautomeric forms of the sulfur-ligands as they resulted from DFT calculations.

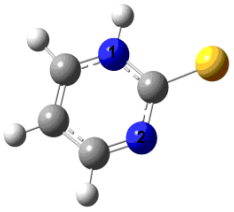
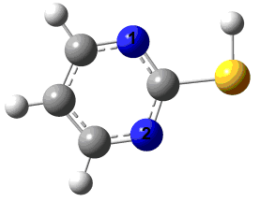
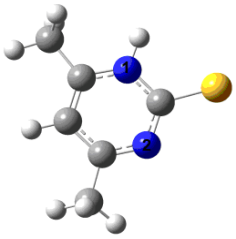
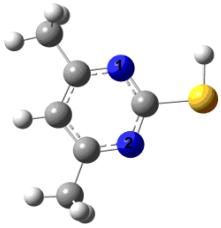
	pymtH$_{thione}$	**pymtH$_{thiol}$**	**dmpymtH$_{thione}$**	**dmpymtH$_{thiol}$**
				
E$_{opt}$, Hartrees	-662.0531	-662.0576	-740.6039	-740.6061
Vacuum	C_{ip}-S_{thione} = 1.65797 Å	-	C_{ip}-S_{thione} = 1.66211 Å	-
	-	C_{ip}-S_{thiol} = 1.76431 Å	-	C_{ip}-S_{thiol} = 1.76804 Å
	-	S_{thiol}-H = 1.34422 Å	-	S_{thiol}-H = 1.34425 Å
	N_1-H = 1.01314 Å	-	N_1-H = 1.01359 Å	-
	C_{ip}-N_1 = 1.39569 Å	C_{ip}-N_1 = 1.33427 Å	C_{ip}-N_1 = 1.39247 Å	C_{ip}-N_1 = 1.33104 Å
	C_{ip}-N_2 = 1.36851 Å	C_{ip}-N_2 = 1.33414 Å	C_{ip}-N_2 = 1.36331 Å	C_{ip}-N_2 = 1.33054 Å
E$_{opt}$, Hartrees	-662.0809	-662.0695	-740.6282	-740.6161
DCM	C_{ip}-S_{thione} = 1.68796 Å	-	C_{ip}-S_{thione} = 1.69165 Å	-
	-	C_{ip}-S_{thiol} = 1.76791 Å	-	C_{ip}-S_{thiol} = 1.77172 Å
	-	S_{thiol}-H = 1.35905 Å	-	S_{thiol}-H = 1.35871 Å
	N_1-H = 1.02878 Å	-	N_1-H = 1.02732 Å	-
	C_{ip}-N_1 = 1.37711 Å	C_{ip}-N_1 = 1.33312 Å	C_{ip}-N_1 = 1.37647 Å	C_{ip}-N_1 = 1.32989 Å
	C_{ip}-N_2 = 1.35548 Å	C_{ip}-N_2 = 1.33455 Å	C_{ip}-N_2 = 1.35012 Å	C_{ip}-N_2 = 1.33126 Å
E$_{opt}$, Hartrees	-662.0846	-662.0709	-740.6316	-740.6174
MeOH	C_{ip}-S_{thione} = 1.69256 Å	-	C_{ip}-S_{thione} = 1.69597 Å	-
	-	C_{ip}-S_{thiol} = 1.76886 Å	-	C_{ip}-S_{thiol} = 1.77251 Å
	-	S_{thiol}-H = 1.36139 Å	-	S_{thiol}-H = 1.36099 Å
	N_1-H = 1.03108 Å	-	N_1-H = 1.02986 Å	-
	C_{ip}-N_1 = 1.37517 Å	C_{ip}-N_2 = 1.33288 Å	C_{ip}-N_1 = 1.37401 Å	C_{ip}-N_1 = 1.32958 Å
	C_{ip}-N_2 = 1.35355 Å	C_{ip}-N_2 = 1.33460 Å	C_{ip}-N_2 = 1.34872 Å	C_{ip}-N_2 = 1.33140 Å

Table S3 Geometrical parameters of the optimized structures for the isolated $[Ag(PPh_3)_2(pymtH)]^+$ (**7**) and $[Ag(PPh_3)_3(pymtH)]^+$ (**5**) and the expected $[Ag(PPh_3)_2(pymtH)_2]^+$ products.

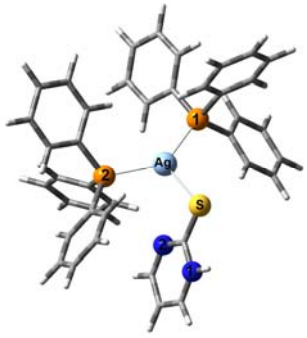
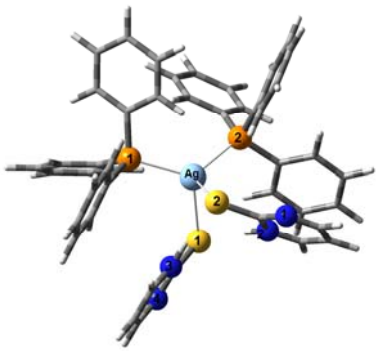
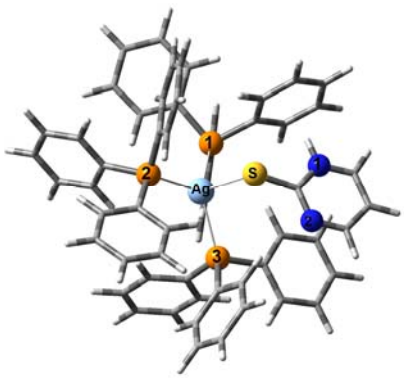
$[Ag(PPh_3)_2(pymtH)]^+$ (7)	**$[Ag(PPh_3)_2(pymtH)_2]^+$**	**$[Ag(PPh_3)_3(pymtH)]^+$ (5)**
		
Ag-S = 2.59843 Å	Ag-S_1 = 2.69371 Å	Ag-S = 2.78708 Å
Ag-P_1 = 2.45015 Å	Ag-S_2 = 2.72814 Å	Ag-P_2 = 2.53540 Å
Ag-P_2 = 2.46475 Å	Ag-P_2 = 2.49245 Å	Ag-P_1 = 2.57620 Å
Ag-N_2 = 3.26057 Å	Ag-P_1 = 2.48423 Å	Ag-P_3 = 2.54077 Å
C_{ip}-S = 1.68331 Å	C_{ip}-S_1 = 1.70525 Å	C_{ip}-S = 1.68567Å
N_1-H = 1.01461 Å	C_{81}-S_2 = 1.70822 Å	C_{ip}-N_1 = 1.37976 Å
C_{ip}-N_1 = 1.37969 Å	C_{ip}-N_3 = 1.37063 Å	C_{ip}-N_2 = 1.35470 Å
C_{ip}-N_2 = 1.35299 Å	C_{ip}-N_4 = 1.34515 Å	S-Ag-P_1 = 103.30°
S-Ag-P_1 = 114.40°	C_{ip}-N_2 = 1.37103 Å	S-Ag-P_2 = 93.00°
S-Ag-P_2 = 113.09°	C_{ip}-N_1 = 1.34379 Å	S-Ag-P_3 = 98.64°
P_1-Ag-P_2 = 132.47°	S_2-Ag-P_2 = 110.67°	P_2-Ag-P_3 = 120.44°
	S_1-Ag-P_2 = 104.14°	P_1-Ag-P_3 = 120.60°
	S_2-Ag-P_1 = 103.71°	P_2-Ag-P_1 = 112.71°
	S_1-Ag-P_1 = 113.17°	
	P_2-Ag-P_1 = 125.51°	

Table S4 Geometrical parameters of the optimized structures for the isolated $[Ag(PPh_3)_3(dmpymtH)]^+$ (**6**) and the expected $[Ag(PPh_3)_2(dmpymtH)_2]^+$ products resulted from DFT calculations.

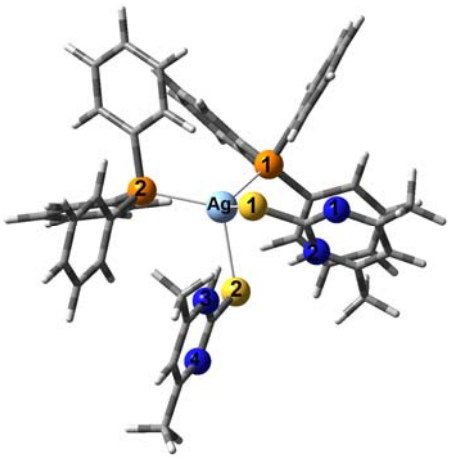
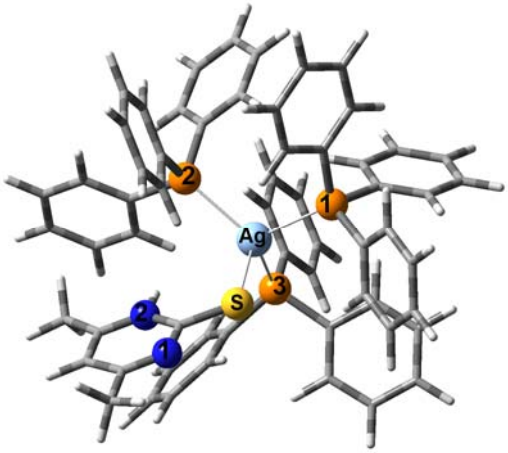
$[Ag(PPh_3)_2(dmpymtH)_2]^+$	$[Ag(PPh_3)_3(dmpymtH)]^+$ (6)
	
$Ag\text{-}S_1$ = 2.69500 Å	Ag-S = 2.66402 Å
$Ag\text{-}S_2$ = 2.69016 Å	$Ag\text{-}P_1$ = 2.56414 Å
$Ag\text{-}P_1$ = 2.50405 Å	$Ag\text{-}P_3$ = 2.55924 Å
$Ag\text{-}P_2$ = 2.50106 Å	$Ag\text{-}P_2$ = 2.54357 Å
$C_{ip}\text{-}S_1$ = 1.71567 Å	C_{ip}-S = 1.69118Å
$C_{ip}\text{-}S_2$ = 1.71206 Å	$C_{ip}\text{-}N_2$ = 1.37695 Å
$C_{ip}\text{-}N_3$ = 1.36829 Å	$C_{ip}\text{-}N_1$ = 1.34763 Å
$C_{ip}\text{-}N_4$ = 1.33826 Å	$S\text{-}Ag\text{-}P_3$ = 106.30°
$C_{ip}\text{-}N_1$ = 1.33402 Å	$S\text{-}Ag\text{-}P_1$ = 95.83°
$C_{ip}\text{-}N_2$ = 1.37085 Å	$S\text{-}Ag\text{-}P_2$ = 110.59°
$S_1\text{-}Ag\text{-}P_1$ = 112.27°	$P_1\text{-}Ag\text{-}P_2$ = 113.29°
$S_2\text{-}Ag\text{-}P_1$ = 107.95°	$P_3\text{-}Ag\text{-}P_2$ = 117.97°
$S_1\text{-}Ag\text{-}P_2$ = 107.39°	$P_1\text{-}Ag\text{-}P_3$ = 110.38°
$S_2\text{-}Ag\text{-}P_2$ = 111.06°	
$P_1\text{-}Ag\text{-}P_2$ = 119.37°	

Table S5 Geometrical parameters for the two Cu^{I}-pymtH-cations resulted from DFT calculations.

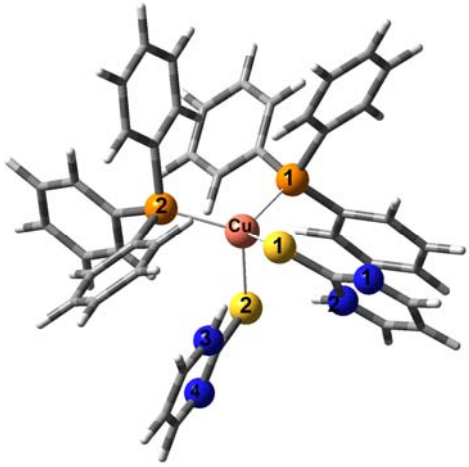
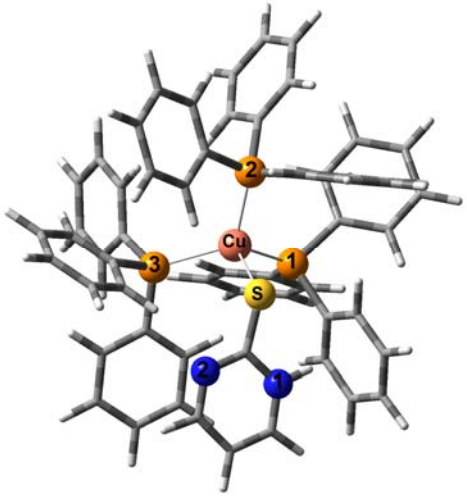
$[Cu(PPh_3)_2(pymtH)_2]^+$ (1)	**$[Cu(PPh_3)_3(pymtH)]^+$ (2)**
	
$Cu\text{-}S_1$ = 2.41485 Å	Cu-S = 2.52914 Å
$Cu\text{-}S_2$ = 2.42846 Å	$Cu\text{-}P_2$ = 2.36001 Å
$Cu\text{-}P_2$ = 2.3381 Å	$Cu\text{-}P_3$ = 2.37649 Å
$Cu\text{-}P_1$ = 2.32289 Å	$Cu\text{-}P_1$ = 2.42174 Å
$C_{ip}\text{-}S_1$ = 1.70402 Å	C_{ip}-S = 1.69243 Å
$C_{ip}\text{-}S_2$ = 1.70895 Å	$C_{ip}\text{-}N_2$ = 1.35194 Å
$C_{ip}\text{-}N_3$ = 1.36960 Å	$C_{ip}\text{-}N_1$ = 1.37706 Å
$C_{ip}\text{-}N_4$ = 1.34322 Å	$S\text{-}Cu\text{-}P_3$ = 101.32°
$C_{ip}\text{-}N_1$ = 1.34557 Å	$S\text{-}Cu\text{-}P_1$ = 103.99°
$C_{ip}\text{-}N_2$ = 1.36917 Å	$S\text{-}Cu\text{-}P_2$ = 95.25°
$S_1\text{-}Cu\text{-}P_1$ = 110.21°	$P_1\text{-}Cu\text{-}P_2$ = 112.12°
$S_2\text{-}Cu\text{-}P_1$ = 102.81°	$P_3\text{-}Cu\text{-}S_{75}$ = 101.32°
$S_1\text{-}Cu\text{-}P_2$ = 104.41°	$P_1\text{-}Cu\text{-}S_{75}$ = 103.99°
$S_2\text{-}Cu\text{-}P_2$ = 112.20°	
$P_1\text{-}Cu\text{-}S_{75}$ = 110.21°	
$P_2\text{-}Cu\text{-}S_{80}$ = 112.20°	

Table S6 Geometrical parameters for the two Cu^{I}-dmpymtH-cations resulted from DFT calculations.

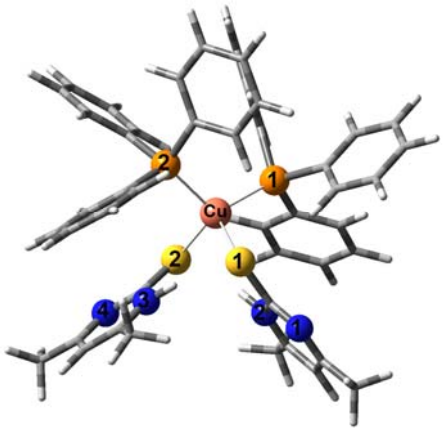
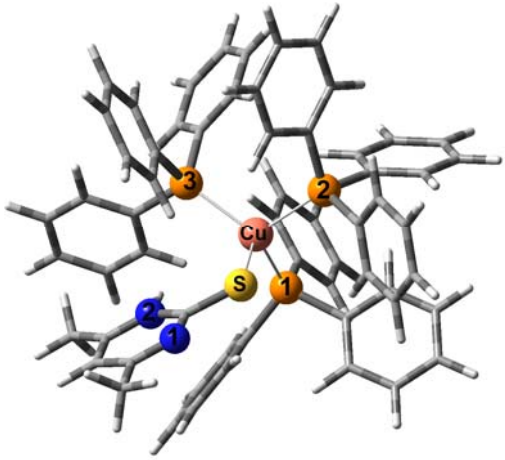
$[Cu(PPh_3)_2(dmpymtH)_2]^+$ (3)	**$[Cu(PPh_3)_3(dmpymtH)]^+$ (4)**
	
$Cu\text{-}S_2$ = 2.41485 Å	Cu-S = 2.41280 Å
$Cu\text{-}S_1$ = 2.42846 Å	$Cu\text{-}P_2$ = 2.39437 Å
$Cu\text{-}P_1$ = 2.3381 Å	$Cu\text{-}P_3$ = 2.37665 Å
$Cu\text{-}P_2$ = 2.32289 Å	$Cu\text{-}P_1$ = 2.40110 Å
$C_{ip}\text{-}S_2$ = 1.70402 Å	C_{ip}-S = 1.69490 Å
$C_{ip}\text{-}S_1$ = 1.70895 Å	$C_{ip}\text{-}N_2$ = 1.37445 Å
$C_{ip}\text{-}N_1$ = 1.33656 Å	$C_{ip}\text{-}N_1$ = 1.34652 Å
$C_{ip}\text{-}N_2$ = 1.36791 Å	$S\text{-}Cu\text{-}P_3$ = 111.76°
$C_{ip}\text{-}N_3$ = 1.36619 Å	$S\text{-}Cu\text{-}P_1$ = 106.98°
$C_{ip}\text{-}N_2$ = 1.33914 Å	$S\text{-}Cu\text{-}P_2$ = 95.22°
$S_1\text{-}Cu\text{-}P_1$ = 113.55°	$P_1\text{-}Cu\text{-}P_2$ = 108.97°
$S_2\text{-}Cu\text{-}P_1$ = 106.60°	$P_3\text{-}Cu\text{-}S$ = 111.76°
$S_1\text{-}Cu\text{-}P_2$ = 103.94°	$P_2\text{-}Cu\text{-}S$ = 95.22°
$S_2\text{-}Cu\text{-}P_2$ = 109.66°	$P_1\text{-}Cu\text{-}S$ = 106.98°
$P_2\text{-}Cu\text{-}S_2$ = 110.21°	
$P_1\text{-}Cu\text{-}S_1$ = 112.20°	

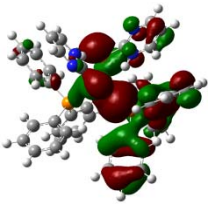
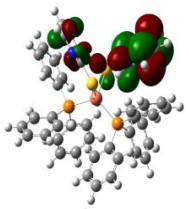
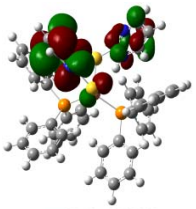
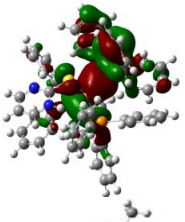
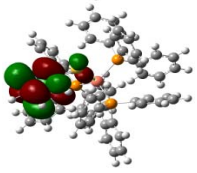
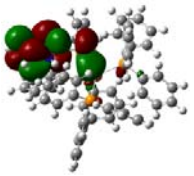
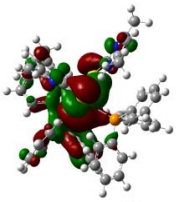
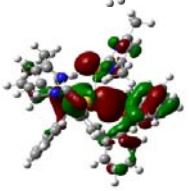
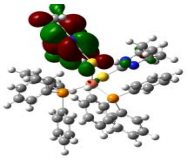
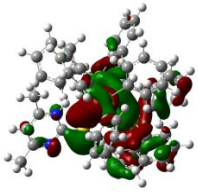
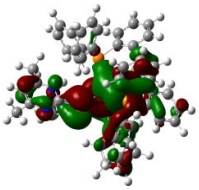
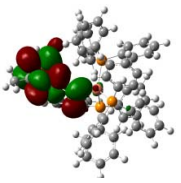
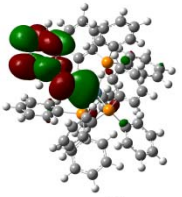
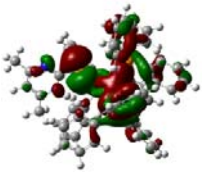
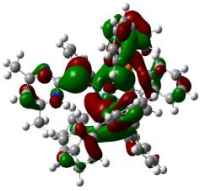
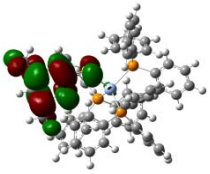
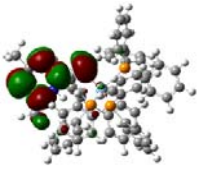
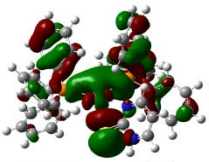
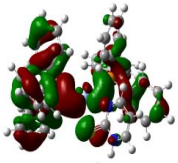
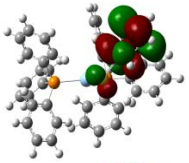
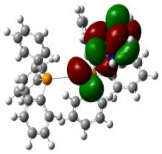
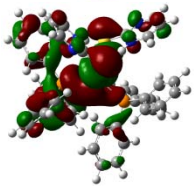
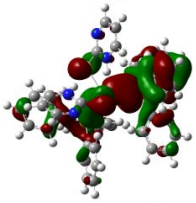
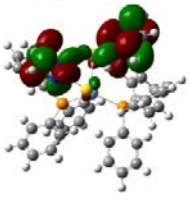
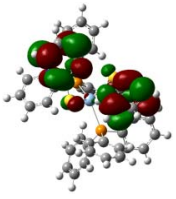
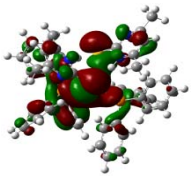
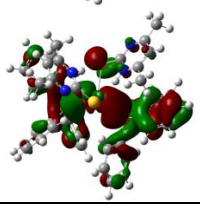
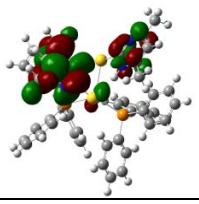
Table S7 NBO atomic charges for the ligands and the studied Ag^{I}-cations.

	q_S	Δq_S [a]	q_{Npyr}	Δq_{Npyr}	q_P	Δq_P [b]	q_{Ag}
pymtH	-0.16	-	-0.46	-	-	-	-
dmpymtH	-0.18	-	-0.49	-	-	-	-
PPh_3	-	-	-	-	+0.91	-	-
$[Ag(PPh_3)_2(pymtH)]^+$ (**7**)	-0.13	+0.03	-0.48	-0.02	+0.95	+0.04	+0.29
$[Ag(PPh_3)_2(pymtH)_2]^+$	-0.17	-0.01	-0.46	+0.00	+0.98	+0.07	+0.019
$[Ag(PPh_3)_3(pymtH)]^+$ (**5**)	-0.17	-0.01	-0.49	-0.03	+0.94 +0.95 +0.95	+0.03 +0.04 +0.04	+0.20
$[Ag(PPh_3)_2(dmpymtH)_2]^+$	-0.20 -0.19	-0.02 -0.01	-0.49	0.00	+0.98	+0.07	+0.03
$[Ag(PPh_3)_3(dmpymtH)]^+$ (**6**)	-0.11	+0.07	-0.49	+0.00	+0.97 +0.97 +0.98	+0.06 +0.06 +0.07	+0.06

[a] Δq_S (= $q_{Scoordinated\ thione} - q_{Sfree\ thione}$) refers to the difference in the nbo charge of the sulfur atom between the coordinated and the respective free thione.

[b] Δq_P (= $q_{Pcoordinated\ phosphine} - q_{Pfree\ phosphine}$) refers to the difference in the nbo charge of the phosphorus atom between the coordinated PPh_3 and the free phosphine.

Table S8 Frontier MOs representation (0.02 isovalue) for the optimized Cu^{I} and Ag^{I} complexes.

Complex cation	HOMO-1	HOMO	LUMO	LUMO+1
$[Cu(PPh_3)_2(pymtH)_2]^+$ (**1**)				
$[Cu(PPh_3)_3(pymtH)]^+$ (**2**)				
$[Cu(PPh_3)_2(dmpymtH)_2]^+$ (**3**)				
$[Cu(PPh_3)_3(dmpymtH)]^+$ (**4**)				
$[Ag(PPh_3)_3(pymtH)]^+$ (**5**)				
$[Ag(PPh_3)_3(dmpymtH)]^+$ (**6**)				
$[Ag(PPh_3)_2(pymtH)]^+$ (**7**)				
$[Ag(PPh_3)_2(pymtH)_2]^+$				
$[Ag(PPh_3)_2(dmpymtH)_2]^+$				

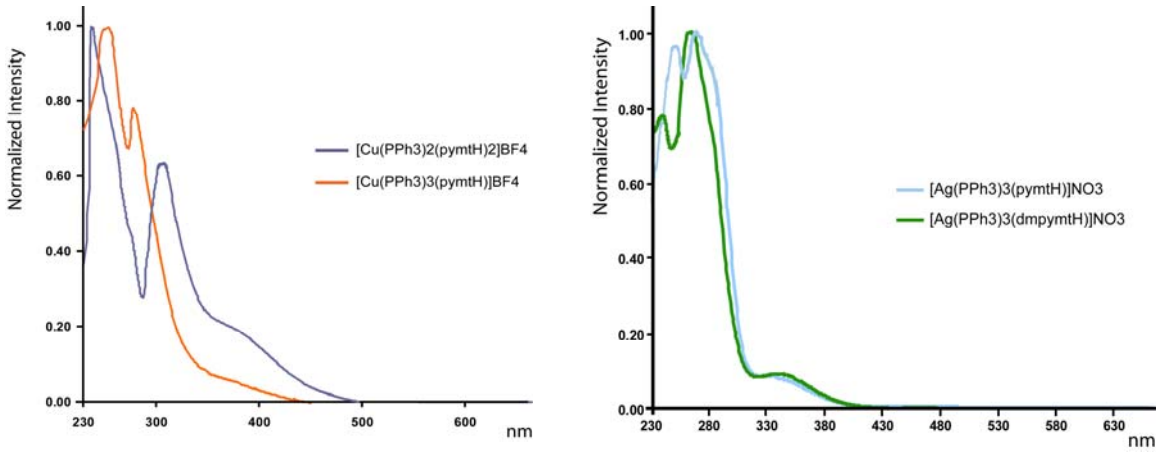


Figure S1. Normalized absorption spectra of Cu^{I}-pymtH complexes (left diagram) and two of the isolated Ag^{I}-complexes (right diagram) in dichloromethane.

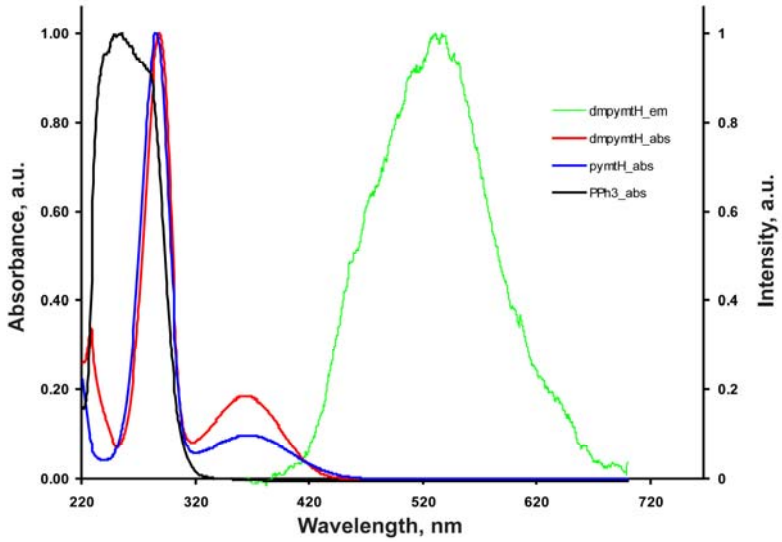


Figure S2. Normalized absorption intensity of PPh_3, pymtH and dmpymtH in dichloromethane and normalized emission intensity of dmpymtH in dichloromethane (λ_{exc} = 350 nm).

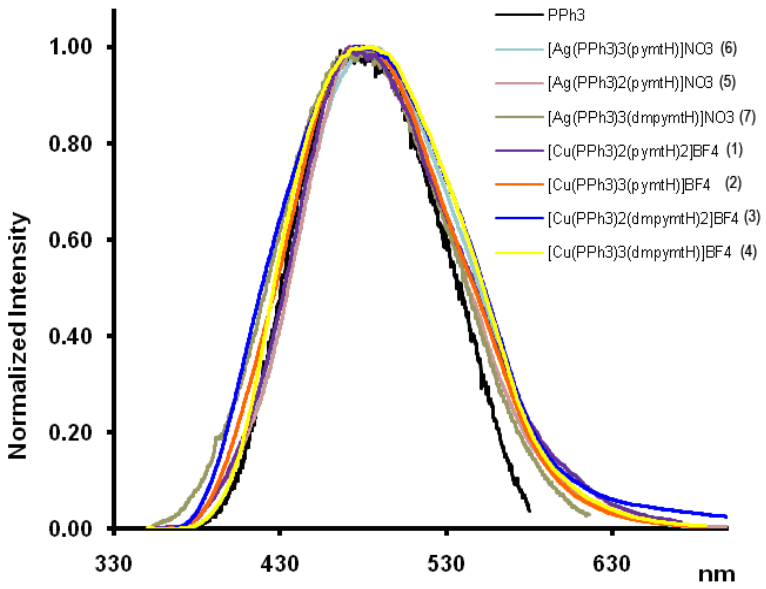


Figure S3. Normalized emission of the Cu(I) and Ag(I) complexes under study in dichloromethane after photoexcitation at 300 nm. Emission of PPh_3 in dichloromethane (black line, λ_{exc} = 300 nm) is also given for comparison reasons.

Excitation	E/eV	λ/nm	Orbital Nature	Character	OS, f
HOMO → LUMO	2.776	447	$3d_{Cu}/\pi_{PPh3} \rightarrow \pi^*_{(pymtH)}$	MLCT/LLCT	0.0014
HOMO → LUMO+1, HOMO-1 → LUMO	2.842	436	$3d_{Cu}/\pi_{PPh3} \rightarrow \pi^*_{(pymtH)}$	MLCT/LLCT	0.0266
HOMO → LUMO+1, HOMO-1 → LUMO+1, HOMO-2 → LUMO+1	2.872	432	$3d_{Cu}/\pi_{PPh3} \rightarrow \pi^*_{(pymtH)}$	MLCT/LLCT	0.0005
HOMO-2 → LUMO	2.930	423	$3d_{Cu} \rightarrow \pi^*_{(pymtH)}$	MLCT	0.0021
HOMO-1 → LUMO+1, HOMO-2 → LUMO+1	3.021	411	$3d_{Cu}/\pi_{PPh3} \rightarrow \pi^*_{(pymtH)}$	MLCT/LLCT	0.0014
HOMO-2 → LUMO+2	3.675	337	$3d_{Cu} \rightarrow \pi^*_{(pymtH)}$	MLCT	0.0227
HOMO-7 → LUMO, HOMO-1 → LUMO+3	3.832	323	$\pi_{PPh3} \rightarrow \pi^*_{(pymtH)}$	LLCT	0.0225
HOMO → LUMO+4	4.367	284	$3d_{Cu}/\pi_{PPh3} \rightarrow \pi^*_{(PPh3)}$	MLCT/IL	0.0968
HOMO-3 → LUMO+3	4.536	273	$3d_{Cu}/\pi_{PPh3}/\pi_{(pymtH)} \rightarrow \pi^*_{(pymtH)}$	MLCT/LLCT/IL	0.0777

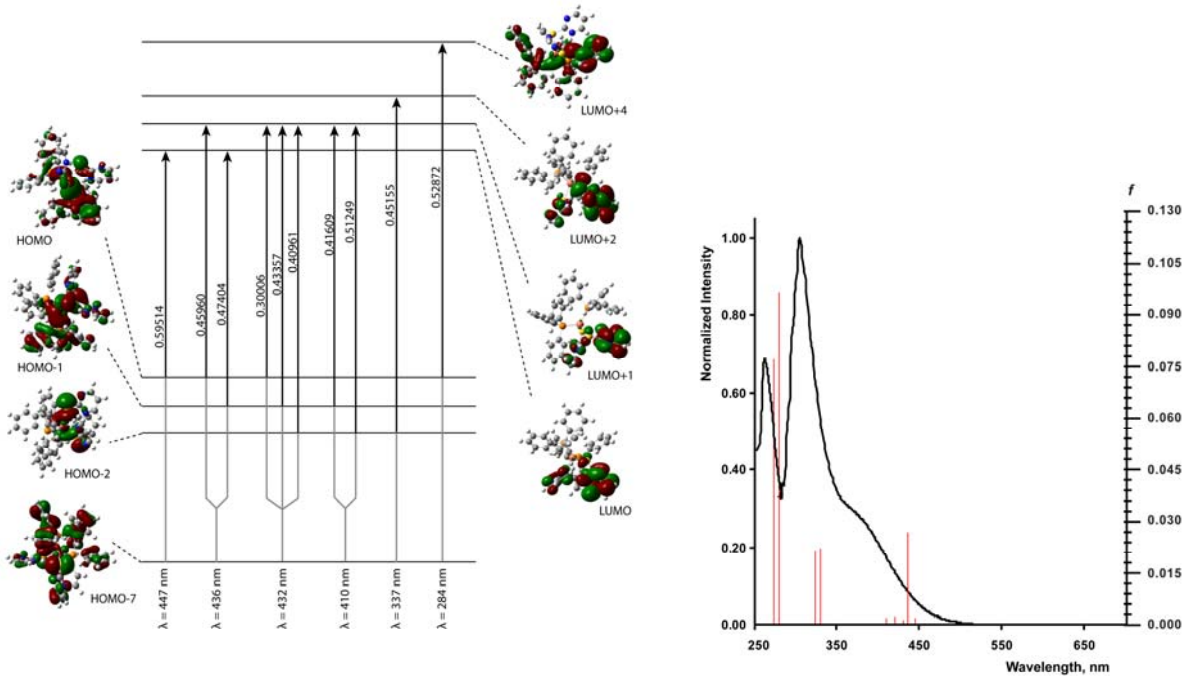


Figure S4 Up: Selected vertical excitations in the absorption spectra of $[Cu(PPh_3)_2(pymtH)_2]^+$ (**1**) calculated at the PBE1PBE/6-31G(d),SDD level of theory. Down left: Representation of MOs of $[Cu(PPh_3)_2(pymtH)_2]^+$ (**1**) involved in selected singlet-singlet transitions along with the calculated excitation wavelengths and CI coefficients. Down right: Experimental absorption spectrum of $[Cu(PPh_3)_2(pymtH)_2]^+$ (**1**) along with the calculated excitation energies appearing as vertical lines.