Supporting Information

Silver alkynyl-phosphine clusters: an electronic effect of the alkynes defines structural diversity

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Table S1. Crystal data and structure refinement for **1–4**, **6–9**.

Identification code	**1**	**2**	**3**	**4**
Empirical formula	$C_{212}H_{169}Ag_{12}F_{18}N_5O_{18}P_{12}S_6$	$C_{104}H_{74}Ag_6F_{18}O_9P_6S_3$	$C_{104}H_{83}Ag_6F_9O_{12}P_6S_3$	$C_{235}H_{208}Ag_{12}F_{18}O_{25}P_{12}$
Formula weight	5274.95	2738.85	2624.92	5440.08
Temperature, K	150(2)	120(2)	120(2)	120(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Trigonal	Monoclinic	Monoclinic
Space group	$P\,2_1/n$	$P\,\bar{3}$	P 2_1/n	P 2_1/n
Unit cell dimensions				
a, Å	19.547(4)	18.4199(10)	22.4230(10)	25.400(4)
b, Å	21.520(4)	18.4199(10)	15.8745(7)	30.627(5)
c, Å	24.334(5)	21.9233(11)	34.3444(15)	30.131(5)
α, °	90	90	90	90
β, °	96.446(4)	90	108.5360(10)	96.935(5)
γ, °	90	120	90	90
Volume, $Å^3$	10172(4)	6441.9(8)	11590.8(9)	23268(7)
Z	2	2	4	4
Density (calc.), Mg/m^3	1.722	1.412	1.504	1.553
Absorption coefficient, mm^{-1}	1.364	1.089	1.198	1.145
F(000)	5244	2704	5216	10896
Crystal size, mm^3	0.584 x 0.315 x 0.217	0.223 x 0.203 x 0.143	0.251 x 0.123 x 0.118	0.172 x 0.159 x 0.135
θ range for data collection, °	1.267 to 28.999	1.858 to 26.992	1.792 to 25.050	1.494 to 29.000
Index ranges	-25<=h<=26, -29<=k<=29, -33<=l<=33	-23<=h<=23, -23<=k<=23, -28<=l<=28	-25<=h<=26, -18<=k<=18, -40<=l<=40	-34<=h<=34, -41<=k<=41, -41<=l<=41

Reflections collected	242740	88413	143364	481835
Independent reflections	27051 [R(int) = 0.0328]	8550 [R(int) = 0.0409]	20495 [R(int) = 0.0429]	61843 [R(int) = 0.0456]
Completeness to θ= 25.242°	100.0 %	89.0 %	99.9 %	99.9 %
Absorption correction	Numerical	Numerical	Numerical	Numerical
Max. and min. transmission	0.756 and 0.503	0.860 and 0.793	0.872 and 0.753	0.861 and 0.827
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	27051 / 171 / 1330	8550 / 126 / 426	20495 / 119 / 1188	61843 / 560 / 3008
Goodness-of-fit on F^2	1.048	1.068	1.085	1.184
Final R indices [I>2sigma(I)][a]	R1 = 0.0286, wR2 = 0.0640	R1 = 0.0483, wR2 = 0.1113	R1 = 0.0715, wR2 = 0.1687	R1 = 0.0847, wR2 = 0.1810
R indices (all data)	R1 = 0.0377, wR2 = 0.0691	R1 = 0.0536, wR2 = 0.1139	R1 = 0.0877, wR2 = 0.1795	R1 = 0.1041, wR2 = 0.1922
Largest diff. peak and hole	2.451 and -1.882 e.Å^{-3}	1.324 and -1.396 e.Å^{-3}	2.545 and -2.341 e.Å^{-3}	3.614 and -2.620 e.Å^{-3}

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S1. Continued.

Identification code	**6**	**7**	**8**	**9**
Empirical formula	$C_{118}H_{117}Ag_7F_{12}O_{21}P_6S_4$	$C_{225}H_{202}Ag_{14}F_{24}N_6O_{27}P_{12}S_8$	$C_{255}H_{252}Ag_{14}F_{18}N_8O_{24}P_{12}S_6$	$C_{108}H_{110}Ag_8F_{12}O_{14}P_6S_4$
Formula weight	3168.26	6016.21	6228.81	3036.97
Temperature, K	120(2)	120(2)	120(2)	120(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Trigonal	Triclinic	Triclinic
Space group	$P\bar{1}$	$R3c$	$P\bar{1}$	$P\bar{1}$

Unit cell dimensions				
a, Å	14.6180(4)	23.0625(6)	16.8626(7)	13.8948(9)
b, Å	20.2170(5)	23.0625(6)	17.5460(8)	14.7416(10)
c, Å	22.3293(6)	39.8602(11)	22.2763(9)	15.8355(11)
α, °	81.4320(10)	90	98.669(2)	112.562(2)
β, °	76.2600(10)	90	91.245(2)	99.276(2)
γ, °	73.0980(10)	120	93.451(2)	94.822(2)
Volume, $Å^3$	6110.6(3)	18360.4(11)	6500.6(5)	2918.1(3)
Z	2	3	1	1
Density (calc.), Mg/m^3	1.722	1.632	1.591	1.728
Absorption coefficient, mm^{-1}	1.330	1.320	1.226	1.544
F(000)	3168	8976	3126	1508
Crystal size, mm^3	0.715 x 0.384 x 0.217	0.430 x 0.382 x 0.372	0.568 x 0.551 x 0.142	0.123 x 0.114 x 0.063
θ range for data collection, °	1.623 to 32.310	2.284 to 32.000	1.604 to 26.000	1.842 to 30.999
Index ranges	-21<=h<=21, -28<=k<=30, -32<=l<=32	-34<=h<=32, -29<=k<=32, -51<=l<=59	-20<=h<=20, -21<=k<=21, -27<=l<=27	-20<=h<=20, -21<=k<=21, -22<=l<=22
Reflections collected	120177	63611	100626	120578
Independent reflections	39049 [R(int) = 0.0282]	12870 [R(int) = 0.0270]	25449 [R(int) = 0.0246]	18515 [R(int) = 0.0467]
Completeness to θ= 25.242°	99.9 %	99.7 %	99.6 %	99.9 %
Absorption correction	Multi-scan	Numerical	Numerical	Multi-scan
Max. and min. transmission	0.761 and 0.450	0.640 and 0.601	0.845 and 0.543	0.909 and 0.833
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	39049 / 0 / 1519	12870 / 67 / 517	25449 / 180 / 1554	18515 / 202 / 737
Goodness-of-fit on F^2	1.012	1.037	1.035	1.042

Final R indices [I>2sigma(I)][a]	R1 = 0.0376, wR2 = 0.0866	R1 = 0.0271, wR2 = 0.0766	R1 = 0.0462, wR2 = 0.1274	R1 = 0.0390, wR2 = 0.1008
R indices (all data)	R1 = 0.0605, wR2 = 0.0976	R1 = 0.0307, wR2 = 0.0791	R1 = 0.0613, wR2 = 0.1415	R1 = 0.0540, wR2 = 0.1068
Largest diff. peak and hole	1.847 and -1.568 e.Å^{-3}	1.354 and -0.558 e.Å^{-3}	2.856 and -1.343 e.Å^{-3}	2.510 and -1.504 e.Å^{-3}

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$.

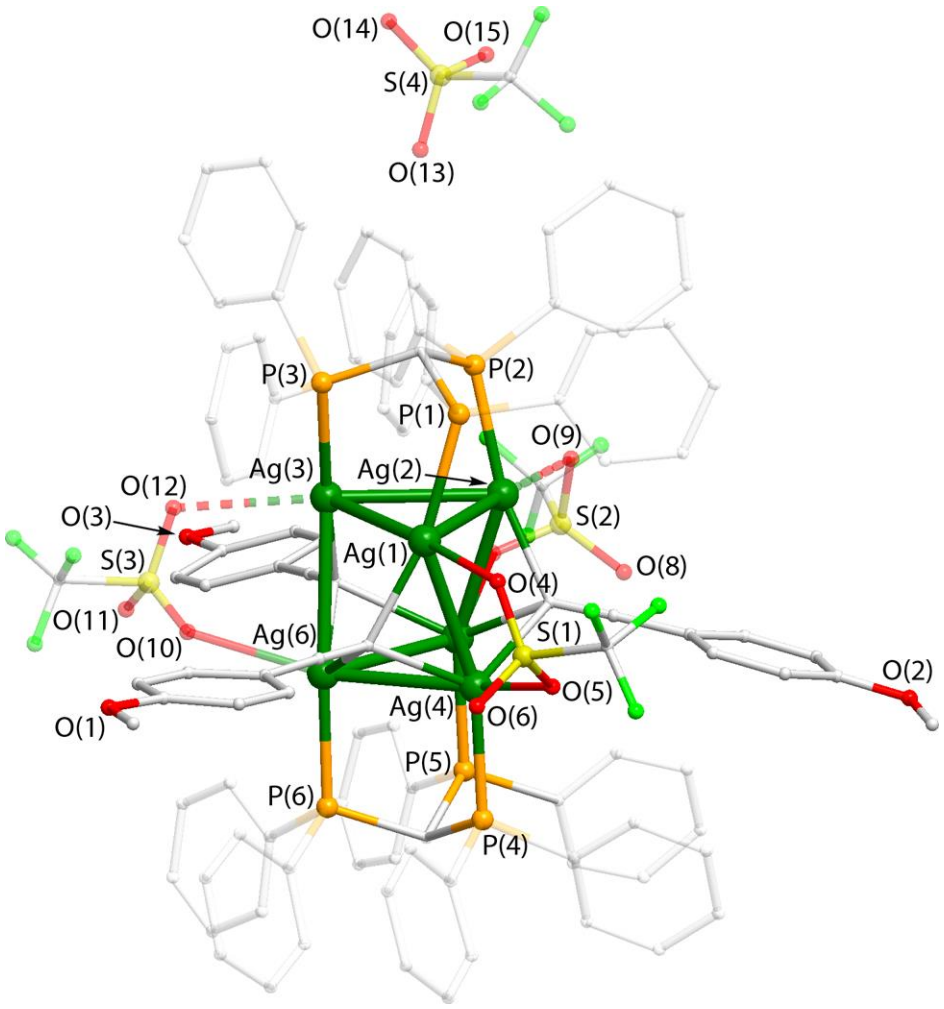


Figure S1. Molecular view of cluster **3**. Two $CF_3SO_3^-$ counterions were placed in three positions (S(2), S(3), S(4)) with occupancies 0.57/0.54/0.89, respectively.

Table S2. Selected interatomic distances (Å) in **1**.

C(1)–Ag(1)	2.160(2)	O(1)–Ag(2)	2.577(2)
C(1)–Ag(4)	2.269(2)	O(3)–Ag(5)	2.732(2)
C(1)–Ag(5)	2.403(2)	O(4)–Ag(1)	2.710(2)
C(9)–Ag(2)	2.179(2)	O(5)–Ag(4)	2.666(2)
C(9)–Ag(5)	2.272(2)	N(1)–Ag(6)	2.446(3)
C(9)–Ag(6)	2.465(2)	Ag(1)–Ag(2)	3.2287(7)
C(17)–Ag(3)	2.135(2)	Ag(1)–Ag(3)	3.0567(5)
C(17)–Ag(4)	2.332(2)	Ag(1)–Ag(4)	2.9782(6)
C(17)–Ag(6)	2.337(2)	Ag(2)–Ag(3)	3.0209(6)
P(1)–Ag(1)	2.3856(7)	Ag(2)–Ag(5)	3.0141(6)
P(2)–Ag(2)	2.4280(8)	Ag(3)–Ag(4)	3.3634(5)

P(3)–Ag(3)	2.3952(8)	Ag(3)–Ag(6)	3.0112(6)
P(4)–Ag(4)	2.4983(8)	Ag(4)–Ag(5)	2.9567(5)
P(5)–Ag(5)	2.4644(8)	Ag(4)–Ag(6)	2.9650(5)
P(6)–Ag(6)	2.4736(8)	Ag(5)–Ag(6)	3.0745(7)

Table S3. Selected interatomic distances (Å) in **2**.

C(1)–Ag(1)	2.281(4)	O(1)–Ag(1)	2.485(3)
C(1)–Ag(2)	2.131(4)	O(2)–Ag(2)	2.940(5)
C(1)–Ag(1´)	2.399(4)	Ag(1)–Ag(2)	3.0142(4)
P(1)–Ag(1)	2.4748(10)	Ag(1)–Ag(1´)	2.9563(5)
P(2)–Ag(2)	2.3845(11)	Ag(2)–Ag(2´)	3.1434(5)

Table S4. Selected interatomic distances (Å) in **3**.

C(1)–Ag(1)	2.149(8)	O(4)–Ag(1)	2.604(8)
C(1)–Ag(4)	2.255(8)	O(5)–Ag(4)	2.542(7)
C(1)–Ag(6)	2.376(8)	O(7)–Ag(5)	2.471(12)
C(10)–Ag(2)	2.116(8)	O(9)–Ag(2)	2.901(14)
C(10)–Ag(5)	2.289(8)	O(12)–Ag(3)	2.757(14)
C(10)–Ag(4)	2.415(8)	O(10)–Ag(6)	2.597(13)
C(19)–Ag(3)	2.145(9)	Ag(1)–Ag(2)	3.0794(9)
C(19)–Ag(5)	2.423(10)	Ag(1)–Ag(3)	3.1315(10)
C(19)–Ag(6)	2.294(10)	Ag(1)–Ag(4)	2.9931(9)
P(1)–Ag(1)	2.391(2)	Ag(2)–Ag(3)	3.1520(9)
P(2)–Ag(2)	2.380(2)	Ag(2)–Ag(5)	2.9798(8)
P(3)–Ag(3)	2.414(2)	Ag(3)–Ag(6)	3.1558(10)
P(4)–Ag(4)	2.473(2)	Ag(4)–Ag(5)	2.9344(9)
P(5)–Ag(5)	2.505(2)	Ag(4)–Ag(6)	3.0222(10)
P(6)–Ag(6)	2.476(2)	Ag(5)–Ag(6)	2.9025(9)

Table S5. Selected interatomic distances (Å) in **4** (two values correspond to the independent molecules found in the unit cell).

C(1)–Ag(1)	2.619(7)	O(4)–Ag(1)	2.512(5)
C(1)–Ag(2)	2.235(7) 2.173(8)	O(5)–Ag(4)	2.408(5) 2.589(8)

C(1)–Ag(4)	2.377(7)	O(6)–Ag(2)	2.413(6)
	2.274(8)		2.482(6)
C(1)–Ag(5)	2.359(7)	O(7)–Ag(5)	2.485(5)
	2.419(8)		2.453(6)
C(10)–Ag(3)	2.184(7)	O(8)–Ag(3)	2.410(6)
	2.300(7)		2.453(6)
C(10)–Ag(5)	2.469(7)	O(9)–Ag(6)	2.452(6)
	2.290(7)		2.406(6)
C(10)–Ag(6)	2.378(7)	Ag(1)–Ag(2)	2.9448(8)
	2.330(8)		3.1414(9)
C(19)–Ag(1)	2.226(8)	Ag(1)–Ag(3)	3.1634(10)
	2.204(7)		3.0803(10)
C(19)–Ag(4)	2.381(8)	Ag(1)–Ag(4)	2.8503(9)
	2.320(7)		2.8732(9)
C(19)–Ag(6)	2.312(8)	Ag(2)–Ag(3)	2.9715(9)
	2.383(7)		2.9912(10)
P(1)–Ag(1)	2.4248(18)	Ag(2)–Ag(5)	2.9615(8)
	2.3826(18)		2.9022(9)
P(2)–Ag(2)	2.4308(17)	Ag(3)–Ag(6)	2.8655(8)
	2.3998(18)		2.8768(8)
P(3)–Ag(3)	2.4389(18)	Ag(4)–Ag(5)	3.0149(8)
	2.4542(18)		2.8896(15)
P(4)–Ag(4)	2.4306(18)	Ag(4)–Ag(6)	2.9726(9)
	2.474(2)		2.9411(10)
P(5)–Ag(5)	2.4544(16)	Ag(5)–Ag(6)	2.9808(9)
	2.4831(19)		3.0158(9)
P(6)–Ag(6)	2.4831(17)		
	2.4374(17)		

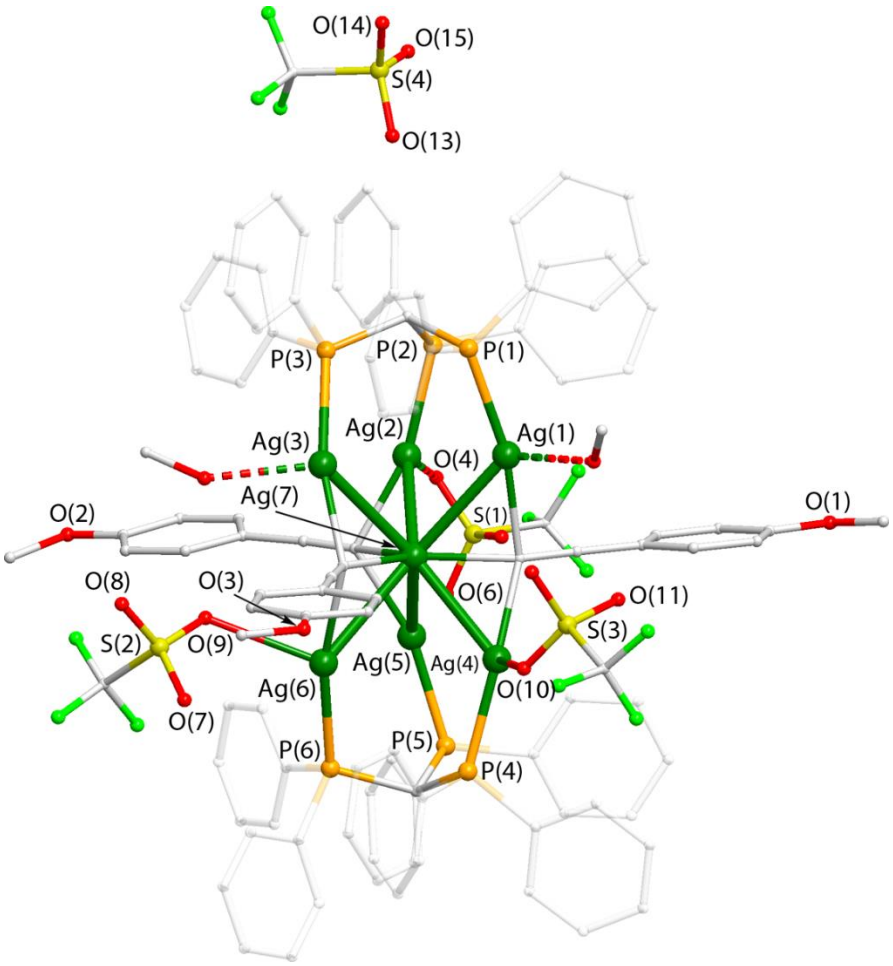


Figure S2. Molecular view of cluster **6**.

Table S6. Selected interatomic distances (Å) in **6**.

C(1)–Ag(1)	2.237(3)	O(4)–Ag(2)	2.816(4)
C(1)–Ag(4)	2.196(3)	O(6)–Ag(5)	2.802(4)
C(1)–Ag(7)	2.181(3)	O(9)–Ag(6)	2.602(4)
C(10)–Ag(2)	2.190(3)	O(10)–Ag(4)	2.524(3)
C(10)–Ag(5)	2.184(3)	O(16)–Ag(3)	2.493(3)
C(10)–Ag(7)	2.287(3)	O(17)–Ag(1)	2.589(3)
C(19)–Ag(3)	2.229(3)	Ag(1)–Ag(7)	2.9264(3)
C(19)–Ag(6)	2.280(3)	Ag(2)–Ag(7)	2.8712(3)
C(19)–Ag(7)	2.229(3)	Ag(3)–Ag(7)	2.8395(3)
P(1)–Ag(1)	2.3890(7)	Ag(4)–Ag(7)	2.8160(3)
P(2)–Ag(2)	2.3711(7)	Ag(5)–Ag(7)	2.8629(3)
P(3)–Ag(3)	2.4094(7)	Ag(6)–Ag(7)	2.9464(3)
P(4)–Ag(4)	2.3871(7)	Ag(1)–Ag(2)	3.4353(5)

P(5)–Ag(5)	2.3746(7)	Ag(1)–Ag(3)	3.8021(6)
P(6)–Ag(6)	2.4401(7)	Ag(2)–Ag(3)	3.4658(5)
		Ag(4)–Ag(5)	3.5272(5)
		Ag(4)–Ag(6)	3.5734(6)
		Ag(5)–Ag(6)	3.5239(5)

Table S7. Selected interatomic distances (Å) in **7**.

C(1)–Ag(1)	2.233(4)	O(1)–Ag(2)	2.570(3)
C(1)–Ag(2)	2.177(4)	O(2)–Ag(1)	2.670(4)
C(1)–Ag(3)	2.240(3)	Ag(1)–Ag(3)	2.8595(4)
P(1)–Ag(1)	2.3712(10)	Ag(2)–Ag(3)	2.8039(4)
P(2)–Ag(2)	2.3790(10)	Ag(1)–Ag(1´)	3.2882(5)
		Ag(2)–Ag(2´)	3.6300(8)

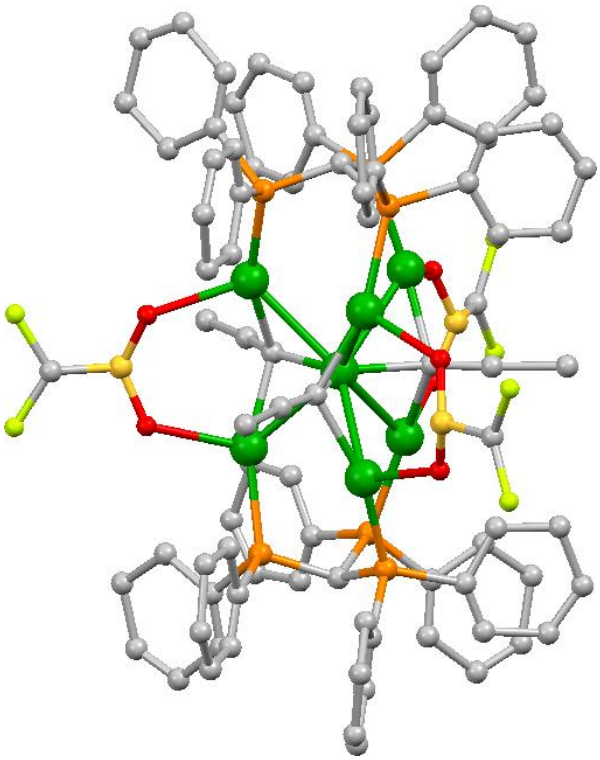


Figure S3. Molecular view of cluster **5**, triflate ions and alkynyl ligands are only partially resolved.

Table S8. Selected interatomic distances (Å) in **8**.

C(1)–Ag(1)	2.439(5)	O(1)–Ag(1)	2.472(3)
C(1)–Ag(2)	2.281(5)	O(2)–Ag(4)	2.494(4)

C(1)–Ag(4)	2.337(5)	Ag(1)–Ag(2)	2.8972(5)
C(1)–Ag(5)	2.380(5)	Ag(1)–Ag(3)	2.9111(5)
C(11)–Ag(1)	2.342(5)	Ag(1)–Ag(4)	2.9249(5)
C(11)–Ag(3)	2.351(5)	Ag(2)–Ag(3)	2.9907(5)
C(11)–Ag(4)	2.550(5)	Ag(2)–Ag(5)	2.9029(5)
C(11)–Ag(6)	2.252(5)	Ag(2)–Ag(7)	2.9839(5)
C(21)–Ag(2)	2.443(5)	Ag(3)–Ag(6)	2.9521(5)
C(21)–Ag(5)	2.388(5)	Ag(3)–Ag(7)	3.0003(5)
C(21)–Ag(7)	2.082(6)	Ag(4)–Ag(5)	2.8796(5)
C(31)–Ag(3)	2.366(5)	Ag(4)–Ag(6)	2.9348(5)
C(31)–Ag(6)	2.494(5)	Ag(5)–Ag(6)	3.0615(5)
C(31)–Ag(7)	2.078(6)	Ag(5)–Ag(7)	2.9831(5)
P(1)–Ag(1)	2.4333(12)	Ag(6)–Ag(7)	3.0598(5)
P(2)–Ag(2)	2.4113(12)		
P(3)–Ag(3)	2.4202(12)		
P(4)–Ag(4)	2.4377(12)		
P(5)–Ag(5)	2.4209(13)		
P(6)–Ag(6)	2.4056(12)		

Table S9. Selected interatomic distances (Å) in **9**.

C(1)–Ag(1)	2.355(3)	O(1)–Ag(1)	2.475(2)
C(1)–Ag(3)	2.362(3)	O(2)–Ag(4)	2.536(2)
C(1)–Ag(4)	2.108(3)	Ag(1)–Ag(3)	2.9829(3)
C(7)–Ag(2)	2.194(4)	Ag(1)–Ag(4)	2.9421(4)
C(7)–Ag(3´)	2.344(3)	Ag(2)–Ag(4)	2.840(2)
C(7)–Ag(4)	2.121(3)	Ag(3)–Ag(4)	2.9879(3)
P(1)–Ag(1)	2.4449(7)	Ag(3)–Ag(4´)	3.0096(3)
P(2)–Ag(2)	2.355(2)		
P(3)–Ag(3)	2.4453(7)		

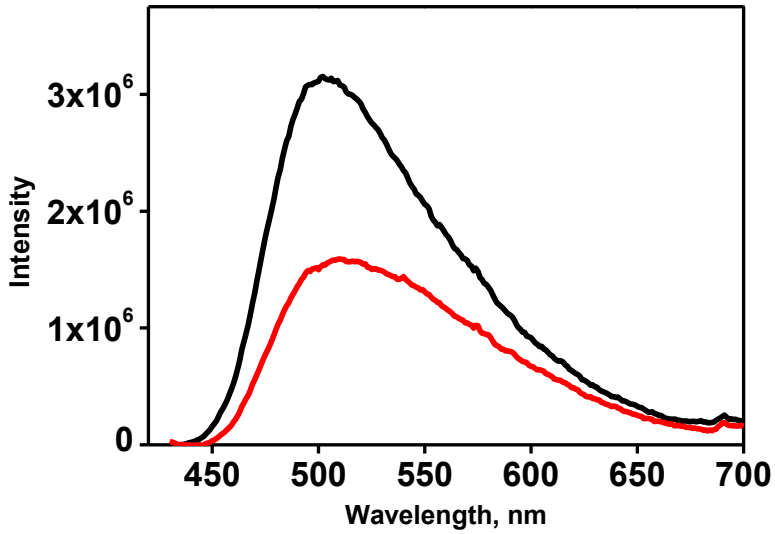
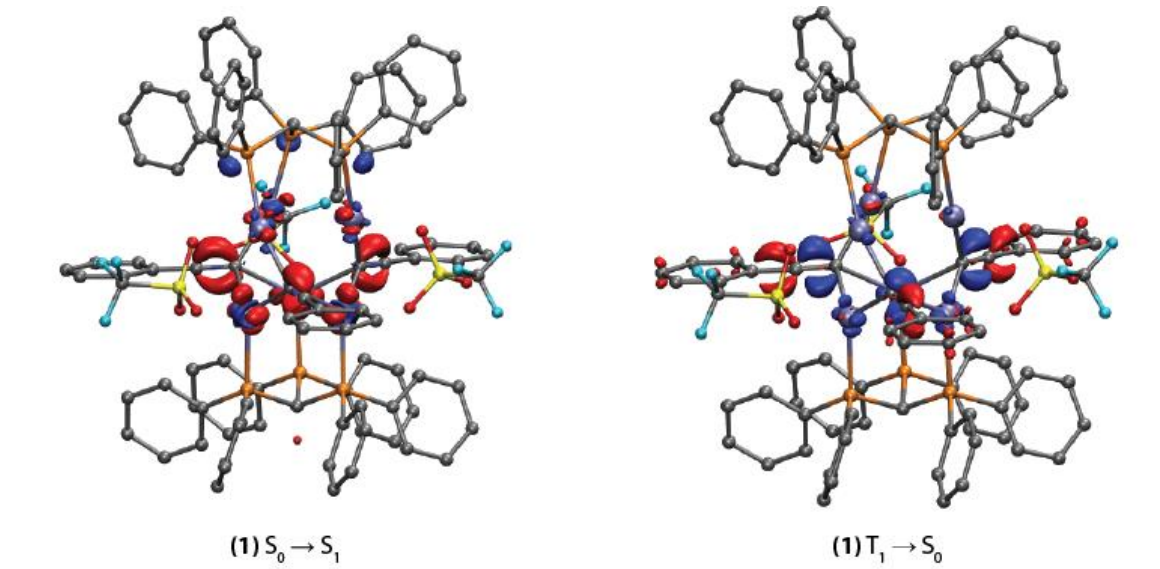
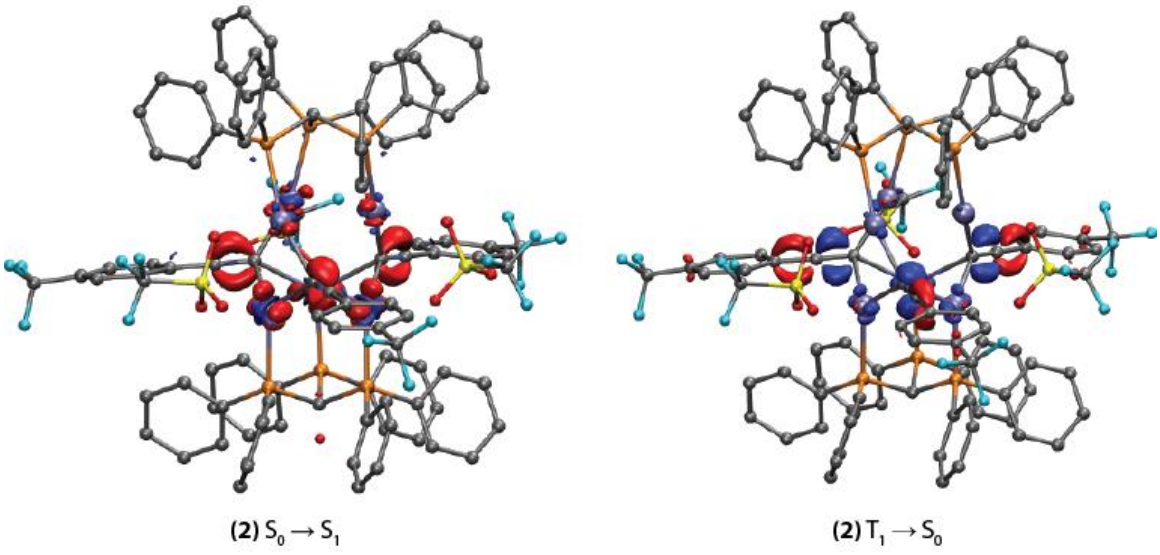


Figure S4. Emission spectra of complex **3** under N_2 (black line) and on air (red line), 298 K.





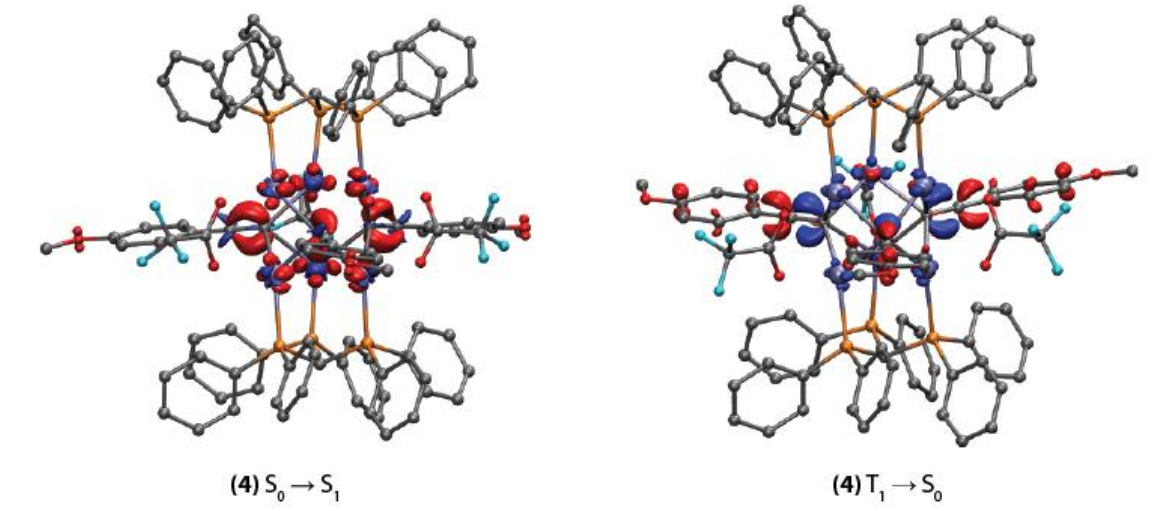


Figure S5. Electron density difference plots for the lowest energy singlet excitation ($S_0 \rightarrow S_1$) and the lowest energy triplet emission ($T_1 \rightarrow S_0$) of the complexes **1, 2** and **4** (isovalue 0.002 a.u.). During the electronic transition, the electron density increases in the blue areas and decreases in the red areas. Hydrogen atoms omitted for clarity.

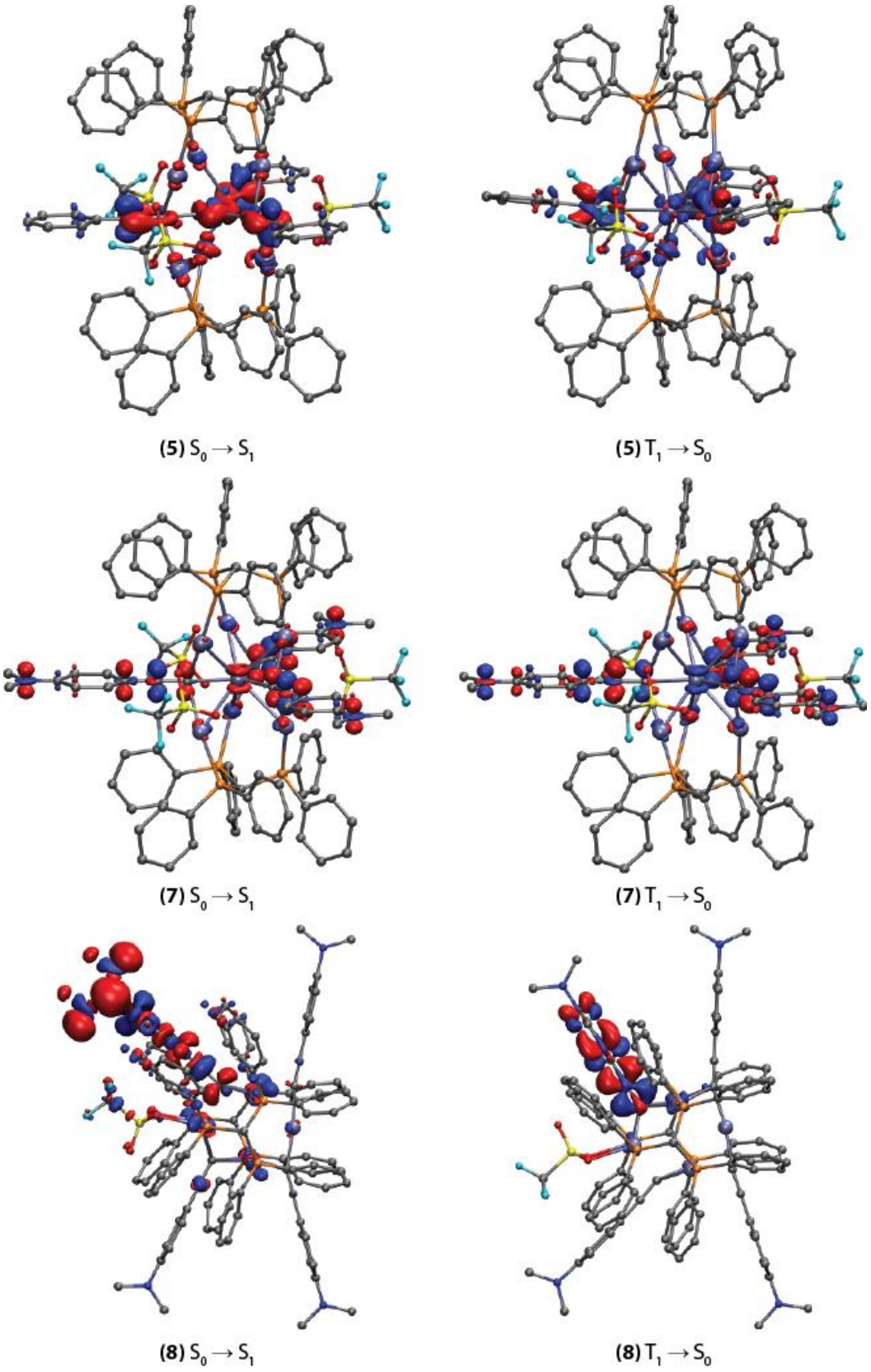


Figure S6. Electron density difference plots for the lowest energy singlet excitation ($S_0 \rightarrow S_1$) and the lowest energy triplet emission ($T_1 \rightarrow S_0$) of the complexes **5**, **7,** and **8** (isovalue 0.002 a.u.). During the electronic transition, the electron density increases in the blue areas and decreases in the red areas. Hydrogen atoms omitted for clarity.