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Supporting information for article:

Luminescence properties and optimized structural conformations of the S0, S1 and T1 states of a tetranuclear formamidinate complex based on Au^{I} and Ag^{I} metal ions

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S1. Geometry

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

S2. Experimental

Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

S3. Refinement

Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger. Crystal Data for **1** (M =625.22 g/mol): tetragonal, space group P-4n2 (no. 118), a = 16.5350(4) Å, c = 18.1127(4) Å, V = 4952.1(3) Å^3, Z = 8, T = 296.15 K, μ(MoKα) = 6.721 mm^{-1}, D_{calc} = 1.677 g/cm^3, 23337 reflections measured (3.336° ≤ 2θ ≤ 56.646°), 5627 unique (R_{int} = 0.0486, R_{sigma} = 0.0464) which were used in all calculations. The final R_1 was 0.0324 (I > 2σ(I)) and wR_2 was 0.0802 (all data).

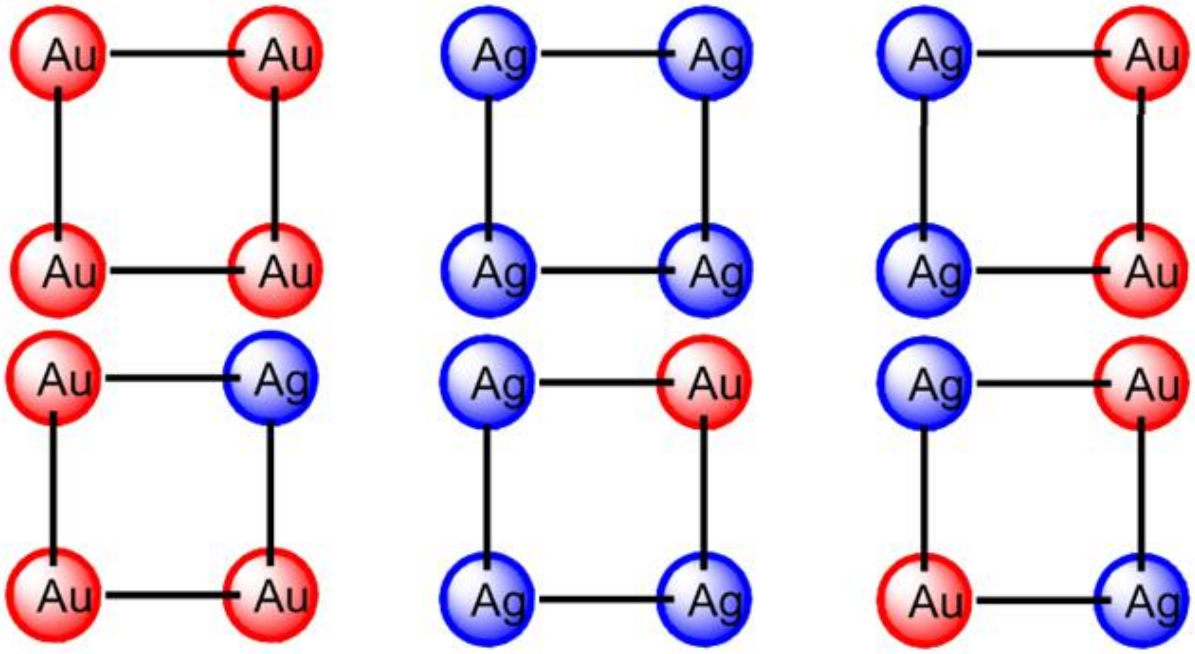

Figure S1 The six possibly structures for complex by Au(I) and Ag(I) disorder.

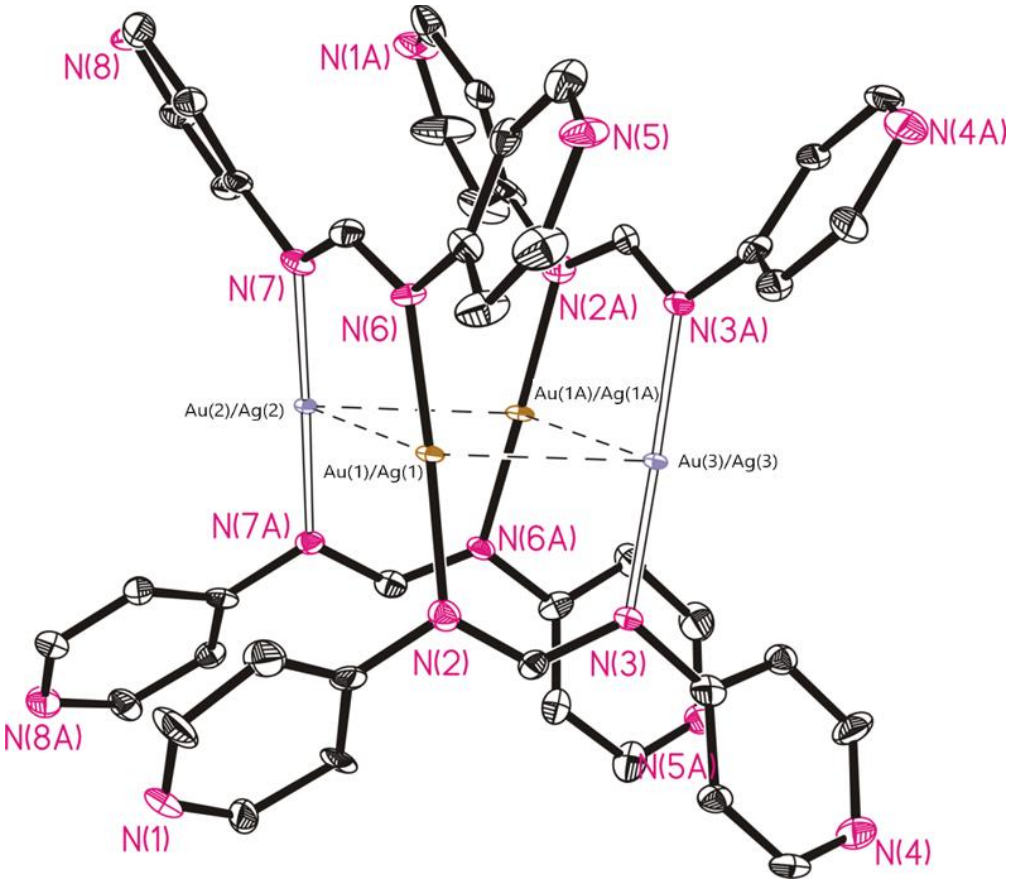

Figure S2 An ORTEP diagram showing the structure **1**.

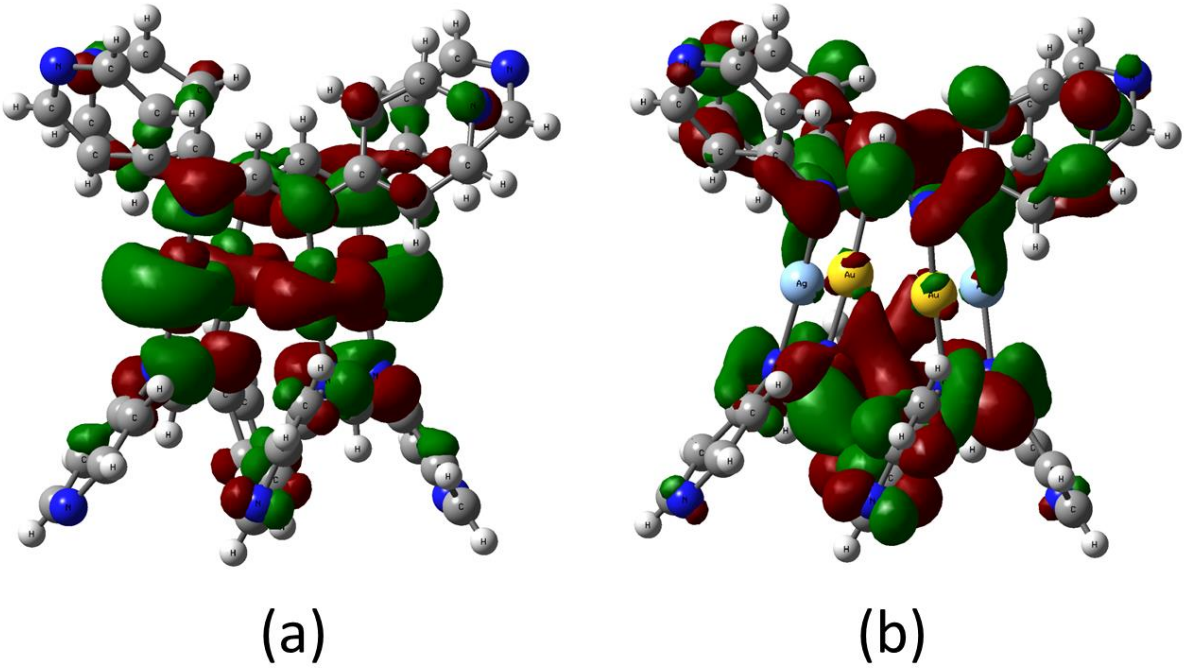

Figure S3. The electron contribution of (a) HOMO and (b) LUMO in complex of $[Au_2Ag_2(4\text{-pyf})_4]$.

Table S1 Crystallographic Data for **1**.

Empirical formula	$C_{22}H_{18}AgAuN_8$
Formula weight	699.28
Temperature/K	296.15
Crystal system	tetragonal
Space group	P-4n2
a/Å	16.5350(4)
b/Å	16.5350(4)
c/Å	18.1127(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4952.1(3)
Z	8
ρ_{calc}g/cm^3	1.876
μ/mm^{-1}	6.733
F(000)	2656.0
Crystal size/mm^3	0.35 × 0.25 × 0.2
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.336 to 56.646
Index ranges	$-16 \le h \le 21$, $-22 \le k \le 21$, $-24 \le l \le 23$
Reflections collected	23337
Independent reflections	5627 [R_{int} = 0.0486, R_{sigma} = 0.0464]
Data/restraints/parameters	5627/0/299
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0771
Final R indexes [all data]	R_1 = 0.0410, wR_2 = 0.0802
Largest diff. peak/hole / e Å^{-3}	1.22/-0.76
Flack parameter	-0.070(14)

Table S2 Luminescent properties of the tetranuclear Au(I) formamidinate clusters and Ag(I) tetranuclear formamidinate complexes.

complex		absorption (nm), (ε = $mol^{-1}dm^3cm^{-1}$)	emission (nm)	excitation (nm)	life time
		$[Au_4(ArNC(H)NAr)_4]$			
1, 4-FC_6H_4	CH_2Cl_2 (RT)	255 (26490), 295 (16584), 325 (12012), 354 (8492), 397 (4528)			
	Solid-state		470	375	737 ns
3,5-$F_2C_6H_3$	CH_2Cl_2 (RT)	255 (18646), 290 (11652), 318 (10732), 353 (4974)			
	Solid-state		478	375	914 ns
2,4,6-$F_3C_6H_2$	CH_2Cl_2 (RT)	253 (73456), 275 (46236), 297 (31352), 355 (3644)			
	Solid-state		508	375	857 ns
2,3,5,6-F_4C_6H	CH_2Cl_2 (RT)	258 (79225), 272 (68865), 293 (47175), 375 (2090)			
	Solid-state		450	375	234 ns
C_6H_4-4-OMe	RT		495, 529	362	2.29 ns
C_6H_4-4-Me	RT		490, 530	359	
C_6H_3-3,5-Cl	RT		489, 525	360	
C_6H_4-3-CF_3	RT		473	365	0.21 ms
$C_{10}H_7$	RT		538 (broad)	375	1.17 ms
C_6F_5	RT		No emit	x	x
4-py	MeOH	208 (20264), 246 (21326), 267 (17096), 320 (4396)	397sh, 494	326	2.54
	Solid-state		494	372	3.89
pm	MeOH	243 (21681), 261 (15302), 301 (11198), 346 (2752)	503	350	1.77
	Solid-state		508	363	2.71
$[Ag_4(pmf)_4]$	MeOH	206 (13359), 275 (6492), 301 (5734)	385, 454sh	293	49.15
	Solid-state		466	403	45.74
This work, **1**	MeOH	206 (19820), 260 (13021), 293 (12615)	438	304	2.31
	Solid-state		501	375	3.37

Table S3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Au(1)	3983(2)	4864(3)	2437.4(17)	20.2(7)
Au(2)	5000	5000	3761.9(3)	15.40(15)
Au(3)	5000	5000	1104.9(3)	16.05(16)
Ag(1)	3991(4)	4910(5)	2442(2)	9.8(10)
Ag(2)	5000	5000	3761.9(3)	15.40(15)
Ag(3)	5000	5000	1104.9(3)	16.05(16)
N(1)	2597(9)	7481(8)	3844(6)	82(4)
N(2)	3841(5)	6071(5)	2241(4)	37(2)
N(3)	4581(6)	6156(5)	1116(4)	35(2)
N(4)	5261(8)	7869(7)	-518(7)	61(3)
N(5)	2953(9)	2021(6)	1164(5)	66(3)
N(6)	4058(5)	3680(5)	2659(5)	37(2)
N(7)	4811(5)	3776(5)	3785(5)	34(2)
N(8)	5755(8)	2375(6)	5546(7)	63(3)
C(1)	2402(11)	6697(10)	3687(10)	100(7)
C(2)	2800(9)	6221(8)	3171(9)	78(5)
C(3)	3433(7)	6532(7)	2766(7)	51(3)
C(4)	3689(8)	7351(8)	2945(6)	50(3)
C(5)	3242(9)	7751(8)	3500(7)	61(4)
C(6)	4131(7)	6464(6)	1658(6)	36(2)
C(7)	5748(9)	7292(8)	-293(8)	63(4)
C(8)	5551(7)	6690(7)	224(6)	43(3)
C(9)	4761(8)	6703(8)	554(6)	37(3)
C(10)	4234(8)	7308(7)	302(6)	45(3)
C(11)	4487(9)	7877(8)	-215(7)	47(3)

C(12)	2673(9)	2792(8)	1298(8)	72(5)
C(13)	3025(8)	3359(9)	1773(7)	62(4)
C(14)	3720(7)	3138(7)	2156(6)	41(3)
C(15)	4068(7)	2360(7)	2012(6)	42(3)
C(16)	3690(9)	1838(8)	1520(7)	59(4)
C(17)	4425(6)	3366(7)	3256(6)	37(3)
C(18)	5081(8)	2154(9)	5179(7)	48(4)
C(19)	4734(7)	2584(7)	4612(6)	40(3)
C(20)	5088(7)	3286(8)	4377(7)	34(3)
C(21)	5815(8)	3526(7)	4742(6)	48(3)
C(22)	6108(9)	3055(8)	5303(7)	60(4)

Table S4 Anisotropic Displacement Parameters ($Å^2×10^3$) for **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1)	13.1(12)	10.1(8)	37.3(13)	1.4(10)	2.9(10)	1.6(7)
Au(2)	12.8(4)	9.4(4)	24.1(3)	0	0	-0.2(3)
Au(3)	13.3(5)	10.2(4)	24.6(3)	0	0	2.7(3)
Ag(1)	10(2)	11.8(19)	7.2(15)	3.9(15)	-5.0(14)	0.4(14)
Ag(2)	12.8(4)	9.4(4)	24.1(3)	0	0	-0.2(3)
Ag(3)	13.3(5)	10.2(4)	24.6(3)	0	0	2.7(3)
N(1)	121(14)	43(8)	80(8)	3(6)	59(8)	21(7)
N(2)	30(5)	38(5)	44(5)	0(4)	5(4)	2(4)
N(3)	41(6)	32(5)	31(4)	3(4)	4(4)	8(4)
N(4)	62(8)	37(7)	84(9)	16(6)	7(7)	1(6)
N(5)	123(13)	15(6)	61(7)	-1(5)	-36(7)	-16(5)
N(6)	35(4)	25(4)	51(6)	7(4)	-13(4)	-3(3)
N(7)	27(5)	31(5)	44(5)	-5(4)	-10(4)	1(4)

N(8)	83(10)	32(6)	73(8)	2(6)	-28(7)	-12(6)
C(1)	96(14)	62(11)	141(16)	22(11)	77(12)	37(9)
C(2)	66(10)	40(8)	127(14)	9(8)	55(10)	13(7)
C(3)	52(7)	36(7)	65(8)	8(6)	8(6)	24(5)
C(4)	49(8)	60(9)	41(6)	-5(6)	-4(6)	26(6)
C(5)	80(11)	57(9)	46(7)	-6(6)	-8(7)	39(7)
C(6)	38(6)	28(6)	44(6)	5(5)	-4(5)	5(5)
C(7)	73(10)	36(7)	78(10)	10(7)	26(8)	6(7)
C(8)	38(7)	38(7)	52(7)	3(5)	9(5)	8(5)
C(9)	39(8)	28(7)	42(6)	-7(5)	1(5)	6(5)
C(10)	42(7)	37(7)	57(8)	0(6)	5(6)	4(5)
C(11)	52(9)	30(7)	60(8)	6(6)	-8(6)	10(6)
C(12)	81(11)	44(8)	92(10)	4(8)	-50(9)	-19(7)
C(13)	59(9)	49(8)	78(10)	4(7)	-33(7)	-14(7)
C(14)	36(6)	37(6)	50(7)	-7(5)	-8(5)	-10(5)
C(15)	36(6)	41(7)	49(7)	-2(5)	-3(5)	-8(5)
C(16)	72(10)	49(8)	58(8)	-4(6)	6(7)	-10(7)
C(17)	30(6)	34(6)	48(7)	1(5)	1(5)	-3(4)
C(18)	42(8)	43(8)	57(8)	12(6)	-2(6)	6(6)
C(19)	41(7)	34(7)	45(6)	-1(5)	-2(5)	-7(5)
C(20)	31(7)	25(7)	46(6)	-3(5)	3(5)	-1(5)
C(21)	58(9)	30(6)	55(7)	4(5)	-19(6)	-8(6)
C(22)	74(10)	47(8)	58(8)	-5(7)	-19(7)	5(7)

Table S5 Bond Lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au(1)	Au(2)	2.938(3)	N(5)	C(12)	1.377(16)
Au(1)	Au(3)	2.950(4)	N(5)	C(16)	1.412(17)

Au(1)	N(2)	2.041(9)	N(6)	C(14)	1.396(12)
Au(1)	N(6)	2.001(9)	N(6)	C(17)	1.345(12)
Au(2)	N(7A)	2.048(9)	N(7)	C(17)	1.336(12)
Au(2)	N(7)	2.048(9)	N(7)	C(20)	1.420(15)
Au(3)	N(3A)	2.033(8)	N(8)	C(18)	1.348(16)
Au(3)	N(3)	2.033(8)	N(8)	C(22)	1.340(17)
Ag(1)	Ag(2)	2.920(5)	C(1)	C(2)	1.388(18)
Ag(1)	Ag(3)	2.944(6)	C(2)	C(3)	1.379(17)
Ag(1)	N(2)	1.969(11)	C(3)	C(4)	1.455(17)
Ag(1)	N(6)	2.074(11)	C(4)	C(5)	1.413(16)
Ag(2)	N(7)	2.048(9)	C(7)	C(8)	1.405(16)
Ag(2)	N(7A)	2.048(9)	C(8)	C(9)	1.437(16)
Ag(3)	N(3A)	2.033(8)	C(9)	C(10)	1.404(16)
Ag(3)	N(3)	2.033(8)	C(10)	C(11)	1.391(16)
N(1)	C(1)	1.37(2)	C(12)	C(13)	1.399(16)
N(1)	C(5)	1.313(17)	C(13)	C(14)	1.391(16)
N(2)	C(3)	1.393(13)	C(14)	C(15)	1.433(16)
N(2)	C(6)	1.329(12)	C(15)	C(16)	1.389(16)
N(3)	C(6)	1.334(12)	C(18)	C(19)	1.375(17)
N(3)	C(9)	1.393(15)	C(19)	C(20)	1.368(17)
N(4)	C(7)	1.312(16)	C(20)	C(21)	1.428(16)
N(4)	C(11)	1.394(18)	C(21)	C(22)	1.370(16)

A: 1-X, 1-Y, Z

Table S6 Bond Angles for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Au(2)	Au(1)	Au(3)	109.63(13)	C(12)	N(5)	C(16)	114.1(10)
N(2)	Au(1)	Au(2)	97.7(3)	C(14)	N(6)	Au(1)	118.2(7)

N(2)	Au(1)	Au(3)	81.3(3)	C(14)	N(6)	Ag(1)	119.0(7)
N(6)	Au(1)	Au(2)	82.9(3)	C(17)	N(6)	Au(1)	124.5(7)
N(6)	Au(1)	Au(3)	101.7(3)	C(17)	N(6)	Ag(1)	123.8(7)
N(6)	Au(1)	N(2)	176.6(4)	C(17)	N(6)	C(14)	117.3(8)
Au(1A)	Au(2)	Au(1)	70.54(15)	C(17)	N(7)	Au(2)	124.0(7)
N(7)	Au(2)	Au(1A)	100.4(3)	C(17)	N(7)	Ag(2)	124.0(7)
N(7A)	A(u2)	Au(1A)	81.6(3)	C(17)	N(7)	C(20)	114.0(9)
N(7A)	Au(2)	Au(1)	100.4(3)	C(20)	N(7)	Au(2)	122.0(7)
N(7)	Au(2)	Au(1)	81.6(3)	C(20)	N(7)	Ag(2)	122.0(7)
N(7)	Au(2)	N(7A)	177.7(5)	C(22)	N(8)	C(18)	115.1(12)
Au(1)	Au(3)	Au(1A)	70.21(14)	N(1)	C(1)	C(2)	124.6(15)
N(3A)	Au(3)	Au(1)	96.6(3)	C(3)	C(2)	C(1)	120.4(14)
N(3A)	Au(3)	Au(1A)	82.5(2)	N(2)	C(3)	C(4)	121.4(11)
N(3)	Au(3)	Au(1A)	96.6(3)	C(2)	C(3)	N(2)	121.8(12)
N(3)	Au(3)	Au(1)	82.5(2)	C(2)	C(3)	C(4)	116.7(11)
N(3A)	Au(3)	N(3)	178.9(4)	C(5)	C(4)	C(3)	116.3(13)
Ag(2)	Ag(1)	Ag(3)	110.3(2)	N(1)	C(5)	C(4)	127.1(14)
N(2)	Ag(1)	Ag(2)	100.0(4)	N(2)	C(6)	N(3)	126.9(10)
N(2)	Ag(1)	Ag(3)	82.5(3)	N(4)	C(7)	C(8)	125.5(14)
N(2)	Ag(1)	N(6)	175.8(5)	C(7)	C(8)	C(9)	118.5(12)
N(6)	Ag(1)	Ag(2)	82.2(3)	N(3)	C(9)	C(8)	119.2(11)
N(6)	Ag(1)	Ag(3)	100.1(3)	N(3)	C(9)	C(10)	124.6(11)
N(7A)	Ag(2)	Ag(1)	98.9(3)	C(10)	C(9)	C(8)	116.1(11)
N(7)	Ag(2)	Ag(1)	83.1(3)	C(11)	C(10)	C(9)	120.9(12)
N(7)	Ag(2)	N(7A)	177.7(5)	C(10)	C(11)	N(4)	122.4(12)
N(3A)	Ag(3)	Ag(1)	97.9(3)	N(5)	C(12)	C(13)	126.1(13)
N(3)	Ag(3)	Ag(1)	81.2(3)	C(14)	C(13)	C(12)	118.3(13)
N(3A)	Ag(3)	N(3)	178.9(4)	N(6)	C(14)	C(15)	122.3(10)

C(5)	N(1)	C(1)	114.5(12)	C(13)	C(14)	N(6)	119.2(10)
C(3)	N(2)	Au(1)	118.2(7)	C(13)	C(14)	C(15)	118.4(10)
C(3)	N(2)	Ag(1)	117.9(7)	C(16)	C(15)	C(14)	119.6(11)
C(6)	N(2)	Au(1)	125.1(7)	C(15)	C(16)	N(5)	123.2(12)
C(6)	N(2)	Ag(1)	125.3(7)	N(7)	C(17)	N(6)	126.6(10)
C(6)	N(2)	C(3)	116.7(9)	N(8)	C(18)	C(19)	125.0(13)
C(6)	N(3)	Au(3)	123.8(7)	C(20)	C(19)	C(18)	119.5(12)
C(6)	N(3)	Ag(3)	123.8(7)	N(7)	C(20)	C(21)	117.5(11)
C(6)	N(3)	C(9)	114.1(9)	C(19)	C(20)	N(7)	125.5(11)
C(9)	N(3)	Au(3)	122.1(7)	C(19)	C(20)	C(21)	116.9(11)
C(9)	N(3)	Ag(3)	122.1(7)	C(22)	C(21)	C(20)	118.8(12)
C(7)	N(4)	C(11)	116.6(12)	N(8)	C(22)	C(21)	124.6(13)

A: 1-X, 1-Y, Z

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **1**.

Atom	*x*	*y*	*z*	U(eq)
H(1)	1972.02	6467.07	3942.61	120
H(2)	2638.27	5687.86	3099.05	93
H(4)	4122.16	7596.66	2707.21	60
H(5)	3425.02	8260.87	3637.65	73
H(6)	4006.33	7011.04	1624.77	44
H(7)	6266.01	7281.06	-491.68	75
H(8)	5924.07	6291.71	350.06	51
H(10)	3707.78	7329.82	483.02	54
H(11)	4126.28	8276.33	-364.02	57
H(12)	2206.72	2949.48	1049.65	87
H(13)	2799.72	3870.23	1830.69	74
H(15)	4543.4	2205.56	2246.72	50

H(16)	3935.38	1343.7	1419.76	71
H(17)	4409.55	2806.51	3305.34	44
H(18)	4832.14	1674.3	5320.5	57
H(19)	4261.65	2399.32	4390.05	48
H(21)	6085.28	3994.85	4600.4	57
H(22)	6584.86	3217.09	5531.4	72

Table S8 Atomic Occupancy for **1**.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
Au(1)	0.5	Au(2)	0.5	Au(3)	0.5
Ag(1)	0.5	Ag(2)	0.5	Ag(3)	0.5

Table S9 Solvent masks information for **1**.

Number	X	Y	Z	Volume	Electron count
1	0.000	0.500	-0.858	541.1	168.3
2	0.500	0.000	-0.688	541.1	168.3