Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Crystal engineering of aurophilic supramolecular architectures and coordination polymers based on butterfly-like Copper-dicyanoaurate complexes: vapochromism, P-T behaviour and multi-metallic cocrystal formation.

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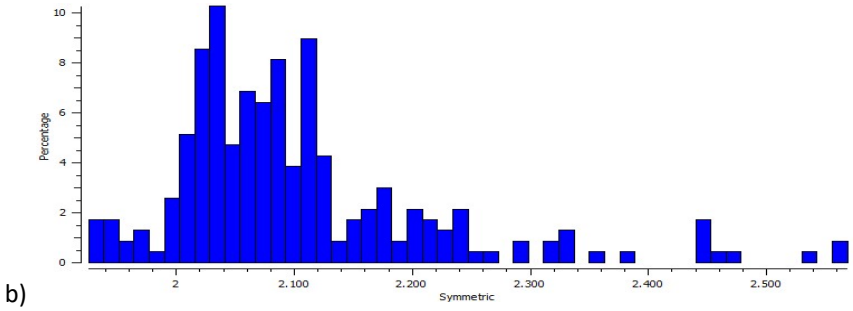
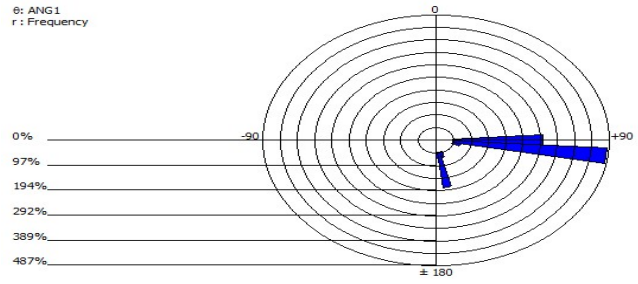
Part 1: Crystallographic, structural and Vibrational data in environmental conditions.

a)

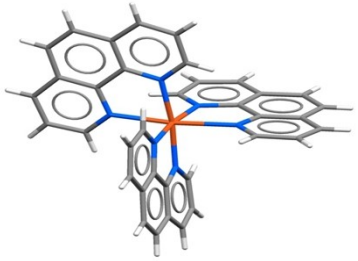


b)



c)

Figure S1: (a) Crystal structure of tris(bipy)Cu(II) complex (in the blue circle bipy with out of plane distortion), (b) distribution of N-Cu distances and (c) N-Cu-N angle circular distribution (from CSD2020).



a)

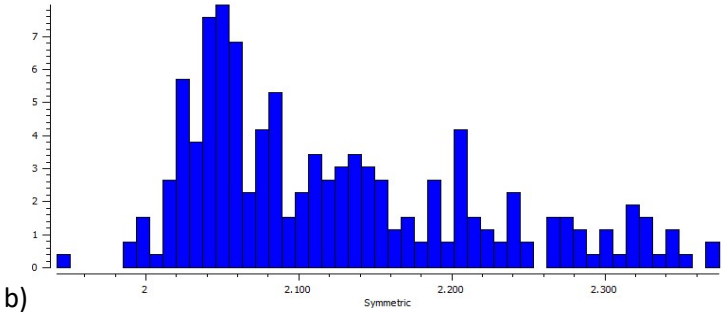
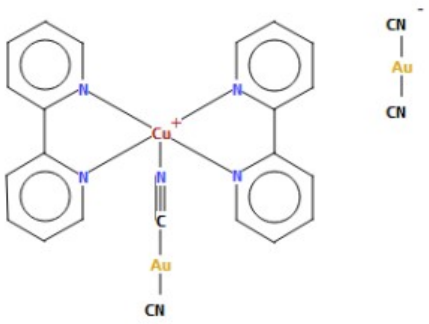
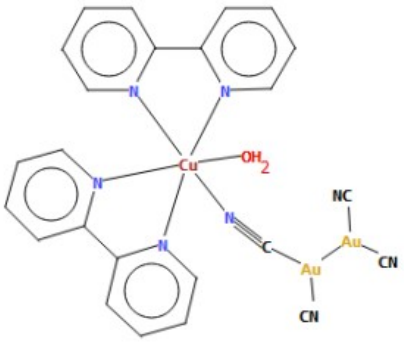


Figure S2: (a) Crystal structure of tris(phen)Cu(II) complex, (b) distribution of N–Cu distances and (c) correlation between N–Cu distances of the same coordinated phen molecules (from CSD2020).



1)



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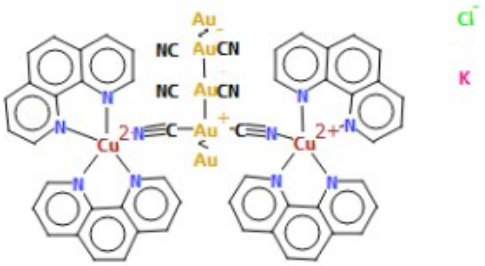

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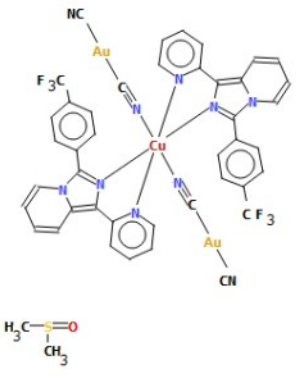

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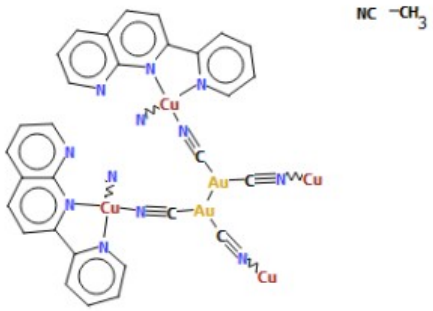
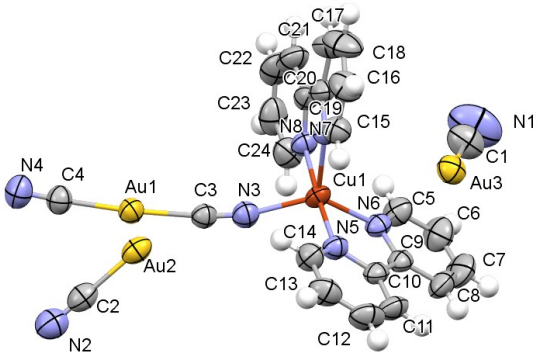


5)

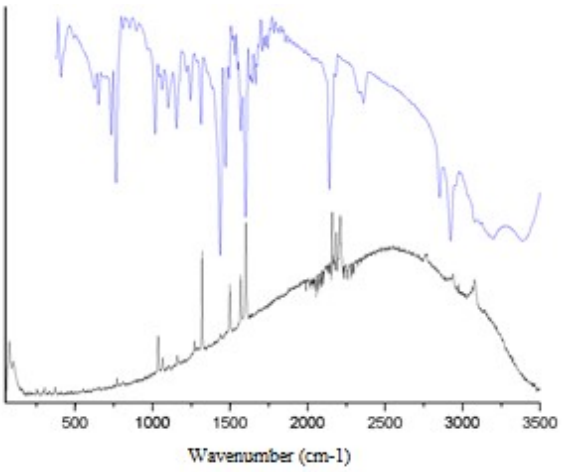
Scheme S1: Formula structures of compound **1**-**5.**

	IR (cm^{-1})	Raman (cm^{-1})
(1)	2196(sh)/ 2185/ 2172/ 2156/2143	2212/2183/2160
(2)	2168/ 2146(sh)	2210/2182/2159
(3)	2197/2166(w)/2131	2212/2151
(4)	2187/2145	2186/2150
(5)	2152	2163
(6)	2153	2156
$K[Au(CN)_2]$	2140	2162/2153

Table S1: ν(CN) frequencies of compound **1**-**6** and $K[Au(CN)_2]$ in IR and Raman spectra.



a)



b)

Figure S3: ORTEP plot (a) of the asymmetric unit (50 % probability) and (b) IR (blue) and Raman (black) spectra of **1.**

Empirical formula	$C_{24}H_{16}Au_2CuN_8$
Formula weight	873.94
Temperature/K	293(2)
Crystal system	Triclinic
Space group	P-1
a/Å	9.9841(3)
b/Å	11.0973(2)

c/Å	12.3344(3)
α/°	98.818(2)
β/°	106.224(2)
γ/°	101.345(2)
Volume/Å^3	1254.67(5)
Z	2
ρ_{calc}g/cm^3	2.313
μ/mm^{-1}	12.533
F(000)	806.0
Crystal size/mm^3	0.521 × 0.324 × 0.119
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.52 to 50.06
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	18190
Independent reflections	4418 [R_{int} = 0.0324, R_{sigma} = 0.0124]
Data/restraints/parameters	4418/0/319
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0214, wR_2 = 0.0542
Final R indexes [all data]	R_1 = 0.0257, wR_2 = 0.0563
Largest diff. peak/hole / e Å^{-3}	1.26/-0.60

Table S2: Crystal data and structure refinement for **1**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Au1	C4	1.979(5)		N7	C15	1.337(6)
Au1	C3	1.994(5)		N8	C24	1.331(6)
Au1	Au2	3.2929(2)		N8	C20	1.331(5)
Au2	C2^1	1.986(6)		C4	N4	1.129(6)
Au2	C2	1.986(6)		C11	C12	1.366(7)
Au2	Au1^1	3.2929(2)		C20	C21	1.388(6)
Au3	C1	1.971(6)		C20	C19	1.480(6)
Au3	C1^2	1.971(7)		C15	C16	1.372(7)
Cu1	N5	1.981(3)		C19	C18	1.381(6)
Cu1	N8	1.997(3)		C2	N2	1.129(6)
Cu1	N3	2.031(4)		C5	C6	1.377(7)
Cu1	N6	2.037(3)		C14	C13	1.387(6)
Cu1	N7	2.120(3)		C13	C12	1.345(7)
N6	C5	1.338(6)		C24	C23	1.377(7)
N6	C9	1.344(5)		C8	C7	1.366(7)
N5	C14	1.323(5)		C16	C17	1.367(8)
N5	C10	1.338(5)		C23	C22	1.358(8)
N3	C3	1.129(5)		C21	C22	1.356(8)
C10	C11	1.396(6)		C6	C7	1.359(7)
C10	C9	1.474(6)		C18	C17	1.379(8)

C9	C8	1.393(6)		N1	C1	1.125(7)
N7	C19	1.342(5)				

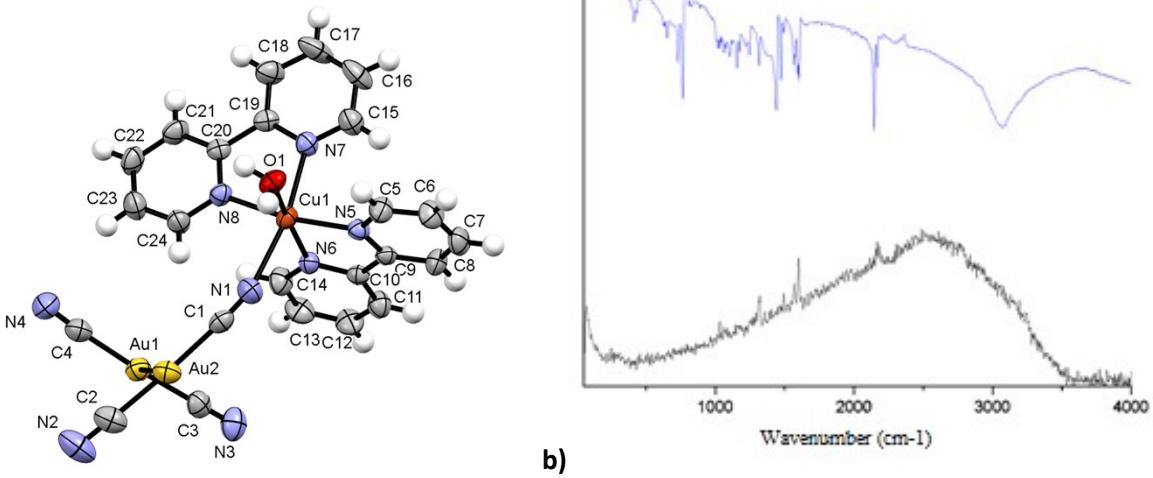
[1]2-X,1-Y,1-Z; [2]2-X,2-Y,-Z

Table S3 Bond Lengths for **1**.

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C4	Au1	C3	175.68(16)		C8	C9	C10	124.5(4)
C4	Au1	Au2	93.46(13)		C19	N7	C15	118.8(4)
C3	Au1	Au2	87.64(11)		C19	N7	Cu1	112.7(3)
C2[1]	Au2	C2	180.000(1)		C15	N7	Cu1	128.1(3)
C2[1]	Au2	Au1	90.25(13)		C24	N8	C20	118.8(4)
C2	Au2	Au1	89.75(13)		C24	N8	Cu1	123.3(3)
C2[1]	Au2	Au1[1]	89.75(13)		C20	N8	Cu1	117.5(3)
C2	Au2	Au1[1]	90.25(13)		N4	C4	Au1	177.1(4)
Au1	Au2	Au1[1]	180.0		C12	C11	C10	119.3(5)
C1	Au3	C1[2]	180.0		N8	C20	C21	120.5(5)
N5	Cu1	N8	176.84(15)		N8	C20	C19	115.1(3)
N5	Cu1	N3	93.22(14)		C21	C20	C19	124.3(4)
N8	Cu1	N3	89.94(14)		N7	C15	C16	123.1(5)
N5	Cu1	N6	80.63(14)		N7	C19	C18	120.8(5)
N8	Cu1	N6	97.28(14)		N7	C19	C20	115.0(4)
N3	Cu1	N6	134.00(14)		C18	C19	C20	124.1(4)
N5	Cu1	N7	99.93(13)		N2	C2	Au2	179.6(5)
N8	Cu1	N7	79.00(13)		N6	C5	C6	122.7(5)
N3	Cu1	N7	106.47(14)		N5	C14	C13	122.2(5)
N6	Cu1	N7	119.52(13)		C12	C13	C14	118.6(5)
C5	N6	C9	118.5(4)		N8	C24	C23	122.9(5)
C5	N6	Cu1	127.5(3)		C13	C12	C11	120.2(4)
C9	N6	Cu1	114.0(3)		C7	C8	C9	119.1(5)
C14	N5	C10	119.7(4)		C17	C16	C15	118.1(5)
C14	N5	Cu1	124.6(3)		C22	C23	C24	118.1(5)
C10	N5	Cu1	115.7(3)		C22	C21	C20	120.1(5)
C3	N3	Cu1	168.0(3)		C7	C6	C5	118.5(5)
N3	C3	Au1	173.4(4)		C6	C7	C8	120.0(5)
N5	C10	C11	120.0(4)		C19	C18	C17	119.6(5)
N5	C10	C9	115.1(3)		C21	C22	C23	119.5(5)
C11	C10	C9	124.8(4)		C16	C17	C18	119.6(5)
N6	C9	C8	121.0(4)		N1	C1	Au3	178.4(8)
N6	C9	C10	114.5(4)					

[1]2-X,1-Y,1-Z; [2]2-X,2-Y,-Z

Table S4: Bond Angles for **1**.



a) b)

Figure S4: ORTEP plot (a) of the asymmetric unit (50 % probability) and (b) IR (blue) and Raman (black) spectra of **2.**

Empirical formula	$C_{24}H_{18}Au_2CuN_8O$
Formula weight	891.94
Temperature/K	298.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.2706(10)
b/Å	14.2900(6)
c/Å	12.7118(10)
α/°	90
β/°	114.476(9)
γ/°	90
Volume/Å^3	2524.6(3)
Z	4
ρ_{calc}g/cm^3	2.347
μ/mm^{-1}	12.462
F(000)	1652.0
Crystal size/mm^3	0.24 × 0.23 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.412 to 59.242
Index ranges	-15 ≤ h ≤ 20, -19 ≤ k ≤ 19, -17 ≤ l ≤ 12
Reflections collected	18791
Independent reflections	7099 [R_{int} = 0.0464, R_{sigma} = 0.0562]
Data/restraints/parameters	7099/0/326
Goodness-of-fit on F^2	0.994
Final R indexes [I>=2σ (I)]	R_1 = 0.0360, wR_2 = 0.0551
Final R indexes [all data]	R_1 = 0.0673, wR_2 = 0.0639
Largest diff. peak/hole / e Å^{-3}	0.63/-0.81

Table S5: Crystal data and structure refinement for **2.**

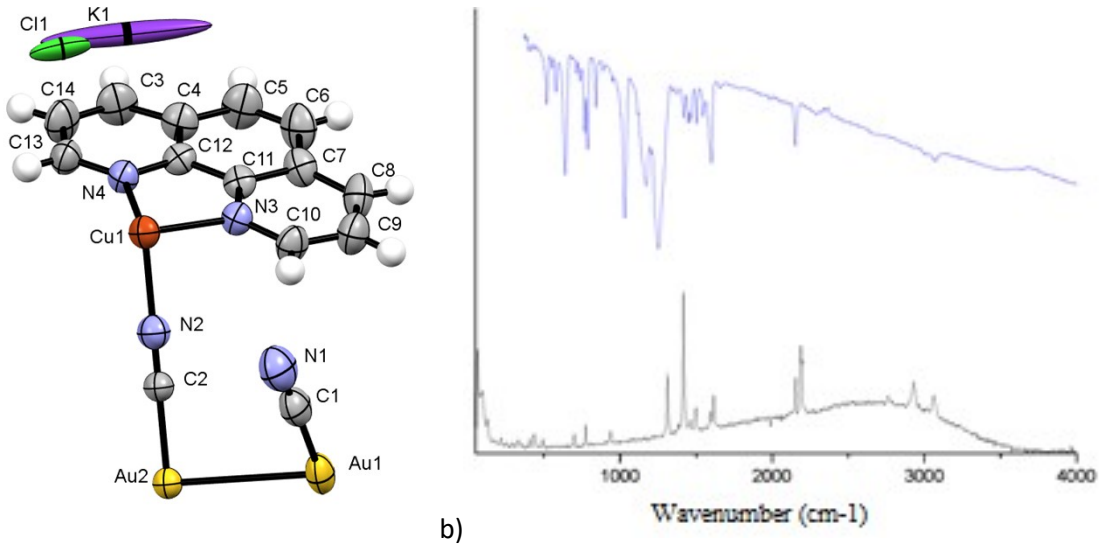
Atom	Atom	Length/Å		Atom	Atom	Length/Å
Au1	Au2	3.2359(4)		C10	C11	1.386(7)
Au1	C4	1.986(7)		C9	C8	1.370(7)
Au1	C3	1.984(7)		C20	C19	1.487(7)
Au2	C1	1.997(6)		C20	C21	1.363(8)
Au2	C2	1.976(7)		C19	C18	1.386(7)
Cu1	N6	2.023(4)		C4	N4	1.123(7)
Cu1	N8	2.058(4)		N3	C3	1.130(7)
Cu1	N7	2.290(4)		C15	C16	1.379(8)
Cu1	N5	2.024(4)		C24	C23	1.365(8)
Cu1	N1	2.418(5)		C14	C13	1.378(8)
Cu1	O1	1.999(4)		C21	C22	1.381(8)
N6	C10	1.347(6)		C5	C6	1.370(8)
N6	C14	1.336(7)		C6	C7	1.370(8)
N8	C20	1.362(6)		C8	C7	1.369(8)
N8	C24	1.333(7)		C23	C22	1.349(8)
N7	C19	1.338(7)		C13	C12	1.361(8)
N7	C15	1.328(7)		C11	C12	1.374(9)
N5	C9	1.344(6)		C18	C17	1.369(9)
N5	C5	1.330(7)		C2	N2	1.147(8)
N1	C1	1.136(7)		C17	C16	1.363(9)
C10	C9	1.470(7)				

Table S6: Bond Lengths for **2**.

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C4	Au1	Au2	85.92(19)		C1	N1	Cu1	157.1(5)
C3	Au1	Au2	96.30(17)		N6	C10	C9	114.8(5)
C3	Au1	C4	175.9(2)		N6	C10	C11	121.3(5)
C1	Au2	Au1	93.61(17)		C11	C10	C9	123.9(5)
C2	Au2	Au1	84.99(19)		N1	C1	Au2	175.0(5)
C2	Au2	C1	177.0(2)		N5	C9	C10	115.1(4)
N6	Cu1	N8	97.27(18)		N5	C9	C8	121.3(5)
N6	Cu1	N7	96.05(16)		C8	C9	C10	123.6(5)
N6	Cu1	N5	80.15(18)		N8	C20	C19	116.3(5)
N6	Cu1	N1	87.61(17)		N8	C20	C21	121.1(5)
N8	Cu1	N7	75.94(16)		C21	C20	C19	122.6(5)
N8	Cu1	N1	93.83(17)		N7	C19	C20	116.1(4)
N7	Cu1	N1	169.47(17)		N7	C19	C18	120.5(5)
N5	Cu1	N8	167.39(16)		C18	C19	C20	123.3(5)

N5	Cu1	N7	91.99(16)		N4	C4	Au1	175.7(5)
N5	Cu1	N1	98.37(17)		N3	C3	Au1	179.5(6)
O1	Cu1	N6	168.86(17)		N7	C15	C16	122.9(6)
O1	Cu1	N8	92.70(17)		N8	C24	C23	122.6(5)
O1	Cu1	N7	91.17(16)		N6	C14	C13	122.3(6)
O1	Cu1	N5	91.16(17)		C20	C21	C22	120.5(6)
O1	Cu1	N1	86.78(17)		N5	C5	C6	122.4(6)
C10	N6	Cu1	114.8(4)		C5	C6	C7	118.1(6)
C14	N6	Cu1	126.5(4)		C7	C8	C9	118.8(5)
C14	N6	C10	118.7(5)		C22	C23	C24	120.4(6)
C20	N8	Cu1	119.0(4)		C12	C13	C14	119.2(6)
C24	N8	Cu1	123.5(4)		C12	C11	C10	119.2(6)
C24	N8	C20	117.5(5)		C17	C18	C19	119.8(6)
C19	N7	Cu1	111.9(3)		C13	C12	C11	119.4(6)
C15	N7	Cu1	128.7(4)		C8	C7	C6	120.2(5)
C15	N7	C19	119.2(5)		C23	C22	C21	117.7(6)
C9	N5	Cu1	114.7(3)		N2	C2	Au2	178.2(7)
C5	N5	Cu1	125.7(4)		C16	C17	C18	119.6(6)
C5	N5	C9	119.2(5)		C17	C16	C15	118.1(6)

Table S7: Bond Angles for **2**.



a) b)

Figure S5: ORTEP plot (a) of the asymmetric unit (50 % probability) and (b) IR (blue) and Raman (black) spectra of **3.**

Empirical formula	$C_{108}H_{64}Au_6Cl_{5.04}Cu_4K_3N_{28}$
Formula weight	3485.86
Temperature/K	293(2)

Crystal system	Orthorhombic
Space group	Fddd
a/Å	9.6024(4)
b/Å	32.1409(14)
c/Å	35.6158(19)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	10992.1(9)
Z	4
ρ_{calc}g/cm^3	2.105
μ/mm^{-1}	9.028
F(000)	6562.7
Crystal size/mm^3	0.63 × 0.23 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.66 to 50.04
Index ranges	-11 ≤ h ≤ 9, -33 ≤ k ≤ 38, -42 ≤ l ≤ 39
Reflections collected	20239
Independent reflections	2437 [R_{int} = 0.0471, R_{sigma} = 0.0264]
Data/restraints/parameters	2437/0/182
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0454, wR_2 = 0.1573
Final R indexes [all data]	R_1 = 0.0551, wR_2 = 0.1665
Largest diff. peak/hole / e Å^{-3}	1.68/-1.23

Table S8: Crystal data and structure refinement for **3.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Au1	C1	1.985(12)		N4	C12	1.356(10)
Au1	C1^1	1.985(12)		C12	C4	1.405(12)
Au1	Au1^2	3.1707(8)		C12	C11	1.415(12)
Au1	Au2	3.2158(4)		C4	C3	1.422(14)
Au2	C2^3	1.971(13)		C4	C5	1.442(13)
Au2	C2	1.971(13)		C11	C7	1.417(12)
Au2	Au1^4	3.2158(4)		C7	C8	1.423(14)
Cu1	N3^4	2.002(6)		C7	C6	1.440(14)
Cu1	N3	2.002(6)		C14	C3	1.340(14)
Cu1	N2	2.037(12)		C14	C13	1.402(14)
Cu1	N4^4	2.074(7)		C9	C8	1.329(15)
Cu1	N4	2.074(7)		C9	C10	1.404(13)
C2	N2	1.111(16)		C5	C6	1.331(14)
N1	C1	1.133(14)		Cl1	Cl1^5	2.35(2)
N3	C10	1.332(11)		K1	K1^6	4.8303(19)
N3	C11	1.350(10)		K1	K1^5	4.830(2)
N4	C13	1.325(11)				

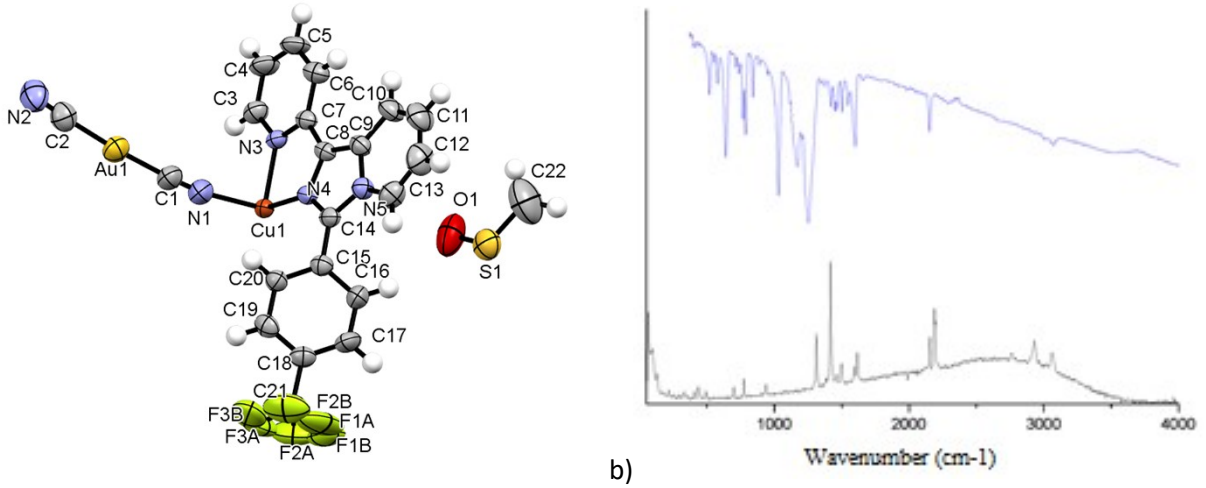
[1]+X,3/4-Y,-1/4-Z; [2]-1/4-X,3/4-Y,+Z; [3]3/4-X,+Y,-1/4-Z; [4]3/4-X,3/4-Y,+Z; [5]5/4-X,+Y,1/4-Z; [6]1/4-X,+Y,1/4-Z

Table S9: Bond Lengths for **5.**

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C1	Au1	C1[1]	178.6(5)		C11	N3	Cu1	113.1(5)
C1	Au1	Au1[2]	90.7(3)		C13	N4	C12	118.2(7)
C1[1]	Au1	Au1[2]	90.7(3)		C13	N4	Cu1	130.8(6)
C1	Au1	Au2	89.3(3)		C12	N4	Cu1	111.0(5)
C1[1]	Au1	Au2	89.3(2)		N4	C12	C4	123.3(8)
Au1[2]	Au1	Au2	180.0		N4	C12	C11	116.8(7)
C2[3]	Au2	C2	180.0		C4	C12	C11	119.8(8)
C2[3]	Au2	Au1[4]	90.0		C12	C4	C3	116.4(8)
C2	Au2	Au1[4]	90.0		C12	C4	C5	119.5(8)
C2[3]	Au2	Au1	90.0		C3	C4	C5	124.0(9)
C2	Au2	Au1	90.0		N3	C11	C12	117.8(7)
Au1[4]	Au2	Au1	180.0		N3	C11	C7	122.2(8)
N3[4]	Cu1	N3	177.8(4)		C12	C11	C7	120.1(8)
N3[4]	Cu1	N2	91.1(2)		C11	C7	C8	116.5(9)
N3	Cu1	N2	91.1(2)		C11	C7	C6	118.3(8)
N3[4]	Cu1	N4[4]	81.3(3)		C8	C7	C6	125.1(8)
N3	Cu1	N4[4]	97.6(3)		C3	C14	C13	120.8(9)
N2	Cu1	N4[4]	118.3(2)		C8	C9	C10	121.7(9)
N3[4]	Cu1	N4	97.6(3)		C9	C8	C7	119.4(9)
N3	Cu1	N4	81.3(3)		N4	C13	C14	121.9(9)
N2	Cu1	N4	118.3(2)		C6	C5	C4	120.5(9)
N4[4]	Cu1	N4	123.5(4)		N3	C10	C9	120.4(9)
N2	C2	Au2	180.000(1)		C5	C6	C7	121.9(9)
C2	N2	Cu1	180.000(1)		C14	C3	C4	119.3(9)
C10	N3	C11	119.6(7)		N1	C1	Au1	176.6(9)
C10	N3	Cu1	127.0(6)		K1[5]	K1	K1[6]	167.4(4)

[1]+X,3/4-Y,-1/4-Z; [2]-1/4-X,3/4-Y,+Z; [3]3/4-X,+Y,-1/4-Z; [4]3/4-X,3/4-Y,+Z; [5]1/4-X,+Y,1/4-Z; [6]5/4-X,+Y,1/4-Z

Table S10: Bond Angles for **3.**



a) b)

Figure S6: ORTEP plot (a) of the asymmetric unit (50 % probability) and (b) IR (blue) and Raman (black) spectra of **4.**

Empirical formula	$C_{44}H_{28}Au_2CuF_6N_{10}OS$
Formula weight	1316.30
Temperature/K	298.00
Crystal system	monoclinic
Space group	C2/c
a/Å	20.8380(15)
b/Å	13.0922(5)
c/Å	16.6160(10)
α/°	90
β/°	103.178(7)
γ/°	90
Volume/Å^3	4413.7(5)
Z	4
ρ_{calc}g/cm^3	1.981
μ/mm^{-1}	7.230
F(000)	2508.0
Crystal size/mm^3	0.35 × 0.21 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.61 to 52.742
Index ranges	-26 ≤ h ≤ 23, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20
Reflections collected	22944
Independent reflections	4518 [R_{int} = 0.0524, R_{sigma} = 0.0455]
Data/restraints/parameters	4518/187/327
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0356, wR_2 = 0.0592
Final R indexes [all data]	R_1 = 0.0640, wR_2 = 0.0679
Largest diff. peak/hole / e Å^{-3}	0.60/-0.75

Table S11: Crystal data and structure refinement for **4.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Au1	C1	1.980(6)		C12	C11	1.387(9)
Au1	C2	1.974(7)		C18	C17	1.378(7)
N4	C14	1.313(5)		C18	C21	1.477(8)
N4	C8	1.356(5)		C3	C4	1.359(7)
N4	Cu1	2.238(3)		C6	C5	1.367(7)
N5	C14	1.373(6)		C4	C5	1.363(7)
N5	C9	1.395(6)		Cu1	N1	2.158(5)
N5	C13	1.393(6)		Cu1	N1[1]	2.158(5)
C7	N3	1.342(5)		C1	N1	1.136(6)
C7	C8	1.452(6)		C2	N2	1.123(7)
C7	C6	1.386(7)		C21	F2A	1.346(12)
N3	C3	1.340(5)		C21	F1A	1.239(12)
N3	Cu1	2.012(4)		C21	F3A	1.315(11)
C14	C15	1.455(6)		C21	F2B	1.336(9)
C20	C15	1.383(6)		C21	F1B	1.322(10)
C20	C19	1.374(7)		C21	F3B	1.287(9)
C9	C8	1.385(6)		F2A	F3A	1.10(3)
C9	C10	1.416(7)		S1	S1[1]	1.312(6)
C15	C16	1.395(6)		S1	O1	1.508(6)
C10	C11	1.336(7)		S1	C22	1.668(9)
C19	C18	1.378(6)		S1	C22[1]	1.742(9)
C16	C17	1.371(7)		F2B	F3B	1.54(2)
C13	C12	1.350(8)				

[1]1-X,+Y,3/2-Z

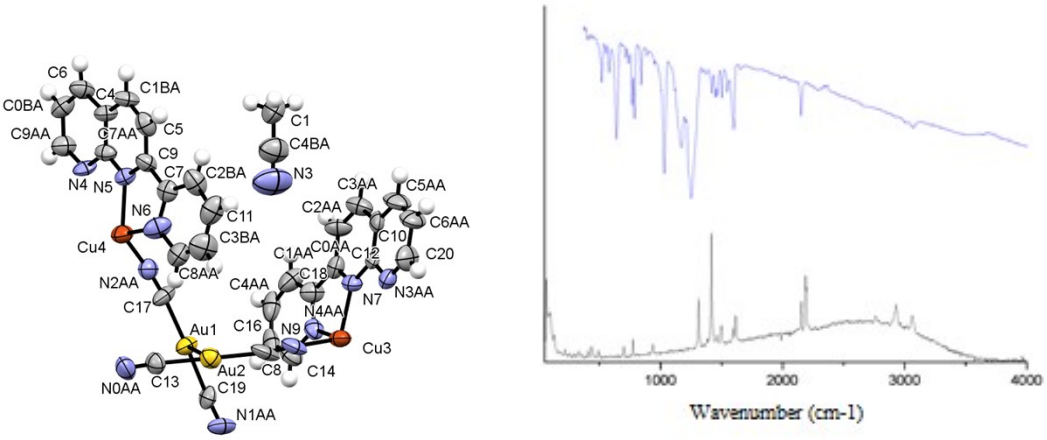
Table S12: Bond Lengths for **4.**

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C2	Au1	C1	176.1(2)		N3[1]	Cu1	N4	100.88(13)
C14	N4	C8	108.4(4)		N3	Cu1	N4	77.90(14)
C14	N4	Cu1	140.9(3)		N3	Cu1	N4[1]	100.88(14)
C8	N4	Cu1	108.1(3)		N3[1]	Cu1	N4[1]	77.90(14)
C14	N5	C9	107.9(4)		N3[1]	Cu1	N3	178.4(2)
C14	N5	C13	130.7(4)		N3	Cu1	N1	88.54(16)
C13	N5	C9	121.1(4)		N3[1]	Cu1	N1[1]	88.54(16)
N3	C7	C8	114.9(4)		N3	Cu1	N1[1]	92.48(16)
N3	C7	C6	120.2(4)		N3[1]	Cu1	N1	92.48(16)
C6	C7	C8	124.9(4)		N1[1]	Cu1	N4	165.67(15)
C7	N3	Cu1	118.7(3)		N1[1]	Cu1	N4[1]	92.08(15)
C3	N3	C7	118.6(4)		N1	Cu1	N4	92.08(15)

C3	N3	Cu1	122.7(3)		N1	Cu1	N4[1]	165.67(15)
N4	C14	N5	109.5(4)		N1	Cu1	N1[1]	98.3(3)
N4	C14	C15	125.9(4)		N1	C1	Au1	175.9(5)
N5	C14	C15	124.6(4)		N2	C2	Au1	175.7(6)
C19	C20	C15	121.0(4)		C1	N1	Cu1	171.0(5)
N5	C9	C10	118.3(4)		F2A	C21	C18	109.0(8)
C8	C9	N5	104.5(4)		F1A	C21	C18	115.3(8)
C8	C9	C10	137.2(5)		F1A	C21	F2A	104.6(13)
N4	C8	C7	118.9(4)		F1A	C21	F3A	130.3(10)
N4	C8	C9	109.7(4)		F3A	C21	C18	113.4(7)
C9	C8	C7	131.4(4)		F3A	C21	F2A	49.0(13)
C20	C15	C14	119.0(4)		F2B	C21	C18	110.2(6)
C20	C15	C16	118.1(5)		F1B	C21	C18	114.8(6)
C16	C15	C14	122.8(4)		F1B	C21	F2B	101.9(7)
C11	C10	C9	119.2(5)		F3B	C21	C18	115.3(7)
C20	C19	C18	120.4(4)		F3B	C21	F2B	71.8(11)
C17	C16	C15	120.6(5)		F3B	C21	F1B	128.3(9)
C12	C13	N5	118.3(5)		F3A	F2A	C21	64.1(10)
C13	C12	C11	121.3(5)		F2A	F3A	C21	67.0(11)
C10	C11	C12	121.6(6)		S1[1]	S1	O1	64.23(14)
C19	C18	C17	119.1(5)		S1[1]	S1	C22[1]	64.4(4)
C19	C18	C21	119.9(5)		S1[1]	S1	C22	70.4(4)
C17	C18	C21	121.0(5)		O1	S1	C22[1]	105.5(4)
C16	C17	C18	120.7(5)		O1	S1	C22	109.2(4)
N3	C3	C4	122.9(5)		C22	S1	C22[1]	99.9(7)
C5	C6	C7	120.5(5)		S1[1]	O1	S1	51.5(3)
C3	C4	C5	119.2(5)		S1	C22	S1[1]	45.2(3)
C4	C5	C6	118.6(5)		C21	F2B	F3B	52.7(6)
N4	Cu1	N4[1]	79.53(17)		C21	F3B	F2B	55.6(7)

[1]1-X,+Y,3/2-Z

Table S13: Bond Angles for **4.**



a) b)

Figure S7: ORTEP plot (a) of the asymmetric unit (50 % probability) and (b) IR (blue) and Raman (black) spectra of **5.**

Empirical formula	$C_{32}H_{21}Au_2Cu_2N_{11}$
Formula weight	1080.61
Temperature/K	295(5)
Crystal system	triclinic
Space group	P-1
a/Å	11.7397(11)
b/Å	12.2661(14)
c/Å	13.3343(17)
α/°	87.894(10)
β/°	75.657(9)
γ/°	64.038(10)
Volume/Å^3	1666.9(4)
Z	2
ρ_{calc}g/cm^3	2.153
μ/mm^{-1}	10.074
F(000)	1012.0
Crystal size/mm^3	0.56 × 0.34 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.544 to 52.744
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	17920
Independent reflections	6808 [R_{int} = 0.0770, R_{sigma} = 0.0868]
Data/restraints/parameters	6808/0/425
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0539, wR_2 = 0.1329
Final R indexes [all data]	R_1 = 0.0992, wR_2 = 0.1903
Largest diff. peak/hole / e Å^{-3}	1.60/-1.09

[1]2-X,-Y,-Z; [2]+X,-1+Y,+Z; [3]1-X,-Y,1-Z

Table S14 Crystal data and structure refinement for **5.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Au1	Au2	3.1340(8)		C0AA	C2AA	1.424(18)
Au1	C17	1.991(13)		C1AA	C4AA	1.39(2)
Au1	C19	2.009(15)		C10	C3AA	1.390(18)
Au2	C13	2.011(13)		C10	C5AA	1.409(19)
Au2	C14	2.006(19)		C3AA	C2AA	1.349(19)
Cu3	N9	2.037(14)		C5AA	C6AA	1.37(2)
Cu3	N1AA[1]	1.893(12)		C20	C6AA	1.39(2)
Cu3	N4AA	2.131(11)		N4	C7AA	1.360(15)
Cu3	N7	2.037(10)		N4	C9AA	1.316(15)
Cu4	N2AA[2]	1.919(12)		N5	C7AA	1.322(15)
Cu4	N0AA[3]	1.964(12)		N5	C9	1.357(15)
Cu4	N5	2.046(10)		N6	C7	1.376(18)
Cu4	N6	2.102(12)		N6	C8AA	1.383(18)
N9	C14	1.076(19)		C7	C9	1.485(17)
C13	N0AA	1.088(16)		C7	C2BA	1.388(18)
C17	N2AA	1.150(16)		C7AA	C4	1.414(16)
C19	N1AA	1.144(16)		C9	C5	1.402(19)
N4AA	C8	1.375(16)		C8AA	C3BA	1.33(2)
N4AA	C18	1.358(17)		C4	C6	1.452(17)
N3AA	C12	1.358(16)		C4	C1BA	1.404(17)
N3AA	C20	1.308(18)		C5	C1BA	1.350(18)
N7	C12	1.353(15)		C6	C0BA	1.361(19)
N7	C0AA	1.348(15)		C9AA	C0BA	1.391(19)
C8	C16	1.36(2)		C2BA	C11	1.35(2)
C12	C10	1.402(17)		C11	C3BA	1.37(2)
C16	C4AA	1.38(2)		C4BA	N3	1.12(2)
C18	C0AA	1.476(18)		C4BA	C1	1.41(3)
C18	C1AA	1.371(18)				

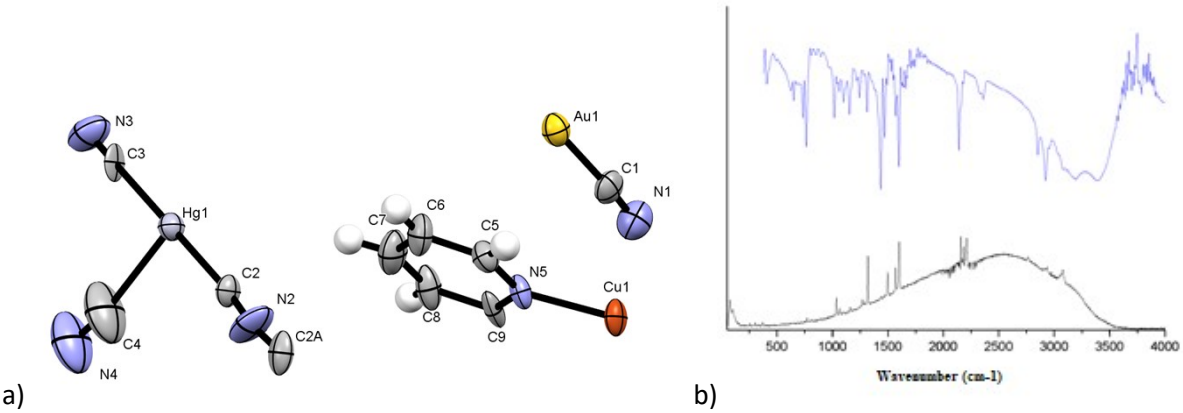
Table S15 Bond Lengths for **5.**

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C17	Au1	Au2	91.3(4)		N7	C0AA	C2AA	121.6(12)
C17	Au1	C19	176.8(6)		C2AA	C0AA	C18	121.6(12)
C19	Au1	Au2	86.8(4)		C18	C1AA	C4AA	119.4(16)
C13	Au2	Au1	88.1(4)		C12	C10	C5AA	116.7(12)
C14	Au2	Au1	92.0(4)		C3AA	C10	C12	117.7(12)
C14	Au2	C13	179.6(6)		C3AA	C10	C5AA	125.4(14)
N9	Cu3	N4AA	100.8(4)		C2AA	C3AA	C10	120.8(13)
N9	Cu3	N7	113.3(5)		C3AA	C2AA	C0AA	118.8(13)

N1AA[1]	Cu3	N9	111.3(5)		C16	C4AA	C1AA	118.1(15)
N1AA[1]	Cu3	N4AA	112.4(5)		C6AA	C5AA	C10	120.8(14)
N1AA[1]	Cu3	N7	130.9(5)		N3AA	C20	C6AA	126.3(15)
N7	Cu3	N4AA	78.1(4)		C9AA	N4	C7AA	119.1(11)
N2AA[2]	Cu4	N0AA[3]	114.7(5)		C7AA	N5	Cu4	125.2(8)
N2AA[2]	Cu4	N5	131.2(4)		C7AA	N5	C9	118.6(11)
N2AA[2]	Cu4	N6	104.9(5)		C9	N5	Cu4	115.9(8)
N0AA[3]	Cu4	N5	105.4(5)		C7	N6	Cu4	114.6(8)
N0AA[3]	Cu4	N6	116.5(5)		C7	N6	C8AA	114.8(13)
N5	Cu4	N6	79.1(4)		C8AA	N6	Cu4	128.7(11)
C14	N9	Cu3	156.9(13)		N6	C7	C9	113.5(11)
N0AA	C13	Au2	176.1(15)		N6	C7	C2BA	121.6(13)
N9	C14	Au2	174.0(15)		C2BA	C7	C9	124.9(14)
N2AA	C17	Au1	172.5(14)		N4	C7AA	C4	121.9(11)
N1AA	C19	Au1	174.1(12)		N5	C7AA	N4	116.0(11)
C17	N2AA	Cu4[4]	160.5(11)		N5	C7AA	C4	122.1(11)
C19	N1AA	Cu3[1]	168.3(13)		N5	C9	C7	116.1(11)
C13	N0AA	Cu4[3]	175.5(15)		N5	C9	C5	121.0(12)
C8	N4AA	Cu3	126.2(10)		C5	C9	C7	122.8(12)
C18	N4AA	Cu3	114.1(8)		C3BA	C8AA	N6	123.8(17)
C18	N4AA	C8	117.4(12)		C5AA	C6AA	C20	116.5(14)
C20	N3AA	C12	116.7(12)		C7AA	C4	C6	117.9(11)
C12	N7	Cu3	125.1(9)		C1BA	C4	C7AA	119.6(11)
C0AA	N7	Cu3	116.3(9)		C1BA	C4	C6	122.3(12)
C0AA	N7	C12	118.3(11)		C1BA	C5	C9	121.8(13)
C16	C8	N4AA	121.5(15)		C0BA	C6	C4	116.9(13)
N3AA	C12	C10	122.9(11)		N4	C9AA	C0BA	122.8(13)
N7	C12	N3AA	114.4(11)		C11	C2BA	C7	120.3(17)
N7	C12	C10	122.7(12)		C6	C0BA	C9AA	121.5(13)
C8	C16	C4AA	120.5(15)		C5	C1BA	C4	116.9(12)
N4AA	C18	C0AA	113.5(11)		C2BA	C11	C3BA	118.8(16)
N4AA	C18	C1AA	122.5(13)		C8AA	C3BA	C11	120.1(17)
C1AA	C18	C0AA	124.0(13)		N3	C4BA	C1	176(3)
N7	C0AA	C18	116.6(12)					

[1]2-X,-Y,-Z; [2]+X,-1+Y,+Z; [3]1-X,-Y,1-Z; [4]+X,1+Y,+Z

Table S16 Bond Angles for **5.**



a) b)

Figure S8: ORTEP plot (a) of the asymmetric unit (50 % probability) and (b) IR (blue) and Raman (black) spectra of **6.**

Empirical formula	$C_{28}H_{16}Au_2CuHg_2N_{12}$
Formula weight	1379.20
Temperature/K	293(2)
Crystal system	Orthorhombic
Space group	Ibam
a/Å	7.7626(13)
b/Å	18.272(2)
c/Å	22.003(3)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	3120.9(8)
Z	4
ρ_{calc}g/cm^3	2.935
μ/mm^{-1}	19.885
F(000)	2460.0
Crystal size/mm^3	0.35 × 0.25 × 0.24
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.8 to 50.04
Index ranges	-7 ≤ h ≤ 9, -17 ≤ k ≤ 21, -23 ≤ l ≤ 26
Reflections collected	6835
Independent reflections	1421 [R_{int} = 0.0588, R_{sigma} = 0.3621]
Data/restraints/parameters	1421/65/121
Goodness-of-fit on F^2	1.099
Final R indexes [I>=2σ (I)]	R_1 = 0.0358, wR_2 = 0.0756
Final R indexes [all data]	R_1 = 0.0478, wR_2 = 0.0814
Largest diff. peak/hole / e Å^{-3}	1.71/-1.28

Table S18 Crystal data and structure refinement for **6.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Hg1	C2	2.07(2)		C9	C9[4]	1.43(2)
Hg1	C3	2.07(2)		C5	C6	1.390(14)
Hg1	C2A[1]	2.10(3)		C6	C7	1.375(16)
Hg1	C4	2.367(19)		C8	C7	1.347(16)
Au1	C1	1.969(13)		C1	N1	1.134(14)
Au1	C1[2]	1.969(13)		N3	C3[7]	0.93(2)
Au1	Au1[3]	3.2324(12)		N3	C3	0.93(2)
Cu1	N5	1.958(8)		N2	C2	0.95(2)
Cu1	N5[4]	1.958(8)		N2	C2A	1.01(3)
Cu1	N5[5]	1.958(8)		C3	C3[7]	1.87(4)
Cu1	N5[6]	1.958(8)		C4	N4[8]	1.04(3)
N5	C5	1.313(12)		C4	C4[8]	1.04(3)
N5	C9	1.368(12)		C2A	Hg1[9]	2.10(3)
C9	C8	1.390(14)				

[1]-1/2+X,1/2-Y,+Z; [2]-X,+Y,1/2-Z; [3]-X,-Y,+Z; [4]1-X,+Y,1/2-Z; [5]1-X,-Y,+Z; [6]+X,-Y,1/2-Z; [7]-X,1-Y,-Z; [8]1-X,1-Y,-Z; [9]1/2+X,1/2-Y,+Z

Table S19: Bond Lengths for **6.**

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
C2	Hg1	C3	179.8(11)		N5	C9	C8	118.7(10)
C2	Hg1	C2A[1]	75.2(13)		N5	C9	C9[4]	115.5(6)
C3	Hg1	C2A[1]	104.9(13)		C8	C9	C9[4]	125.7(7)
C2	Hg1	C4	95.6(11)		N5	C5	C6	122.7(10)
C3	Hg1	C4	84.2(10)		C7	C6	C5	117.0(11)
C2A[1]	Hg1	C4	170.9(12)		C7	C8	C9	120.3(10)
C1	Au1	C1[2]	173.2(6)		N1	C1	Au1	174.4(10)
C1	Au1	Au1[3]	93.4(3)		C8	C7	C6	120.9(11)
C1[2]	Au1	Au1[3]	93.4(3)		C3[7]	N3	C3	180.0(18)
N5	Cu1	N5[4]	83.8(4)		C2	N2	C2A	170(4)
N5	Cu1	N5[5]	104.3(4)		N2	C2	Hg1	174(3)
N5[4]	Cu1	N5[5]	149.5(5)		N3	C3	C3[7]	0.0(9)
N5	Cu1	N5[6]	149.5(5)		N3	C3	Hg1	179(2)
N5[4]	Cu1	N5[6]	104.3(4)		C3[7]	C3	Hg1	179(2)
N5[5]	Cu1	N5[6]	83.8(4)		N4[8]	C4	C4[8]	0.0(11)
C5	N5	C9	120.3(8)		N4[8]	C4	Hg1	169(4)
C5	N5	Cu1	127.0(6)		C4[8]	C4	Hg1	169(4)
C9	N5	Cu1	112.4(6)		N2	C2A	Hg1[9]	174(3)

[1]-1/2+X,1/2-Y,+Z; [2]-X,+Y,1/2-Z; [3]-X,-Y,+Z; [4]1-X,+Y,1/2-Z; [5]1-X,-Y,+Z; [6]+X,-Y,1/2-Z; [7]-X,1-Y,-Z; [8]1-X,1-Y,-Z; [9]1/2+X,1/2-Y,+Z

Part 2: Vapochromism measurements.

Figure S9: Apparatus for the measurement of vapochromism

Part 3: High pressure SCXRD Measurements on 1.

Identification code	**1**	**1**	**1**	**1**
Pressure/GPa	0.1(1)	1.0(1)	1.3(1)	1.6(1)
Empirical formula	$C_{24}H_{16}Au_2CuN_8$	$C_{24}H_{16}Au_2CuN_8$	$C_{24}H_{17}Au_2CuN_8$	$C_{24}H_8Au_2CuN_8$
Formula weight	873.92	873.92	874.93	865.86
Temperature/K	298.0	298.00	298.0	298.00
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.916(2)	9.688(2)	9.640(6)	9.645(5)
b/Å	10.950(3)	10.331(2)	10.225(7)	10.125(6)
c/Å	12.278(2)	12.372(3)	12.417(8)	12.395(6)
α/°	98.765(19)	97.57(2)	97.79(7)	96.68(5)
β/°	105.877(17)	104.512(19)	103.42(6)	104.09(5)
γ/°	101.38(2)	102.93(2)	104.21(7)	104.23(5)
Volume/Å^3	1226.7(4)	1145.0(4)	1130.0(10)	1118.0(10)
Z	2	2	2	2
ρ_{calc}g/cm^3	2.366	2.535	2.572	2.572
μ/mm^{-1}	12.820	13.733	13.918	14.066
F(000)	806.0	806.0	808.0	790.0
Crystal size/mm^3	0.15 × 0.14 × 0.11	0.15 × 0.14 × 0.11	0.15 × 0.14 × 0.11	0.15 × 0.14 × 0.11
Radiation λ /Å	MoKα 0.71073	MoKα 0.71073	MoKα 0.71073	MoKα 0.71073
2Θ range for data collection/°	6.576 to 32.136	3.47 to 34.058	3.444 to 32.052	3.448 to 31.852
Index ranges	-7 ≤ h ≤ 7 -5 ≤ k ≤ 5 -9 ≤ l ≤ 9	-7 ≤ h ≤ 7 -5 ≤ k ≤ 5 -10 ≤ l ≤ 10	-6 ≤ h ≤ 7 -4 ≤ k ≤ 4 -9 ≤ l ≤ 9	-6 ≤ h ≤ 6 -4 ≤ k ≤ 4 -9 ≤ l ≤ 9
Reflections collected	1623	1465	681	666
Independent refl. R_{int} R_{sigma}	390 0.1521 0.1135	370 0.1623 0.1256	226 0.2559 0.2273	224 0.2633 0.2691
Data/restraints/param.	390/70/26	370/86/26	226/129/12	224/159/9
Goodness-of-fit on F^2	1.127	1.131	1.033	1.169
Final R indexes I≥ 2σ (I)	R_1 = 0.0874 wR_2 = 0.1978	R_1 = 0.0994 wR_2 = 0.2185	R_1 = 0.1601 wR_2 = 0.3583	R_1 = 0.1856 wR_2 = 0.3703
Final R indexes all data	R_1 = 0.1023 wR_2 = 0.2056	R_1 = 0.1126 wR_2 = 0.2264	R_1 = 0.2059 wR_2 = 0.3884	R_1 = 0.2352 wR_2 = 0.4134
Largest diff. peak/hole / e Å^{-3}	0.58/-0.70	0.67/-0.66	0.90/-0.84	1.22/-0.90

Table S20 Crystal data and structure refinement for **1** at the different pressures**.**

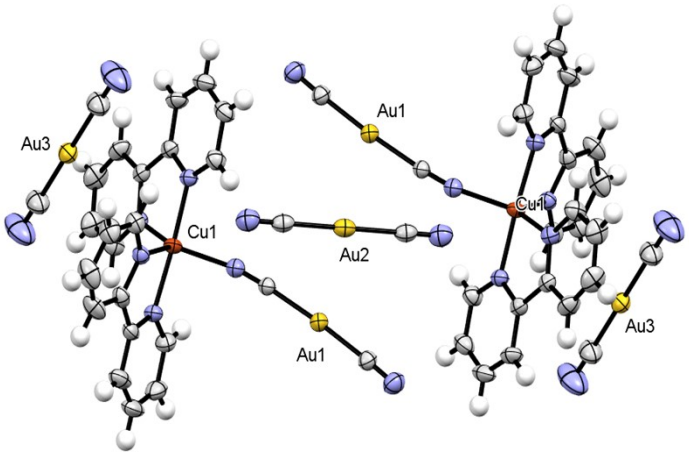
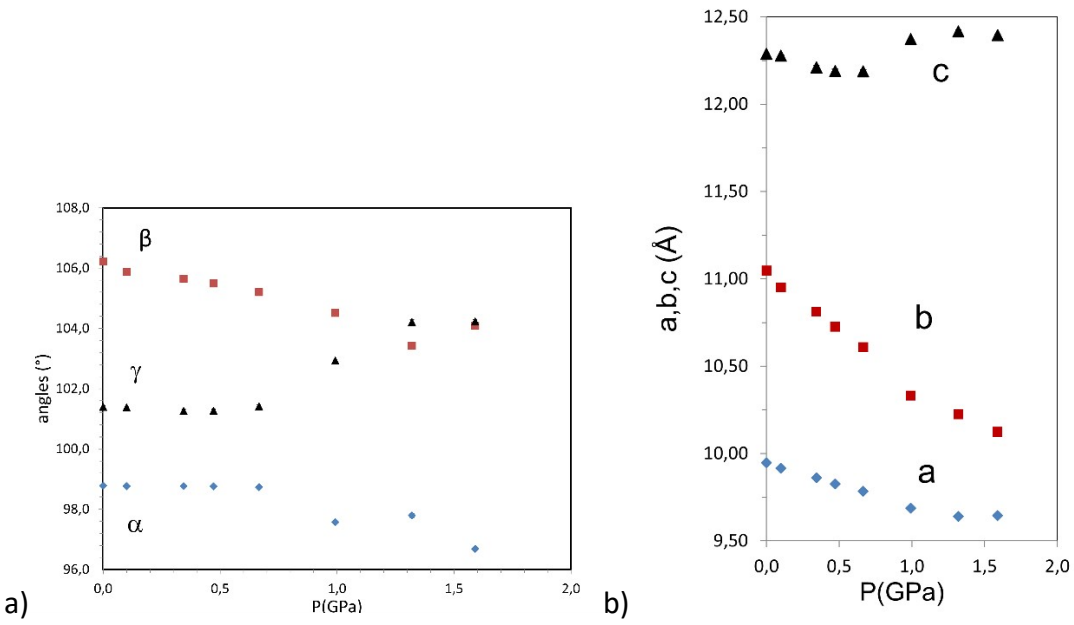
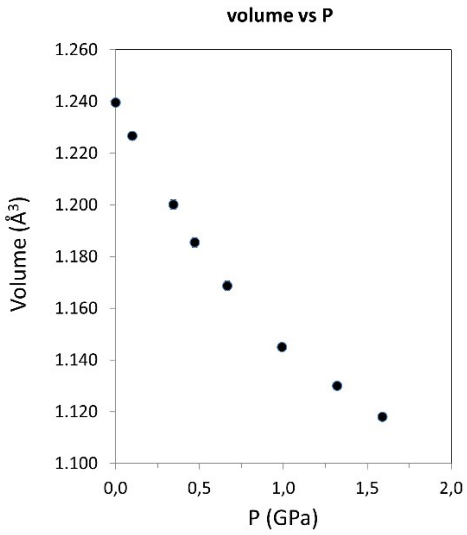


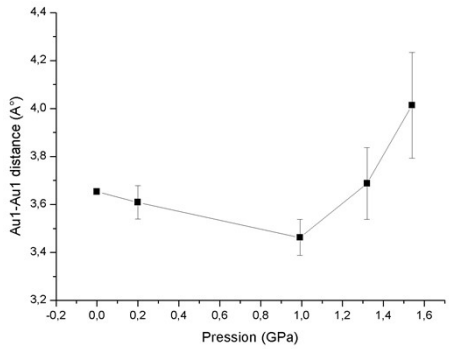
Figure S10: Model of **1** with the numeration of heavy metal atoms for clarity.



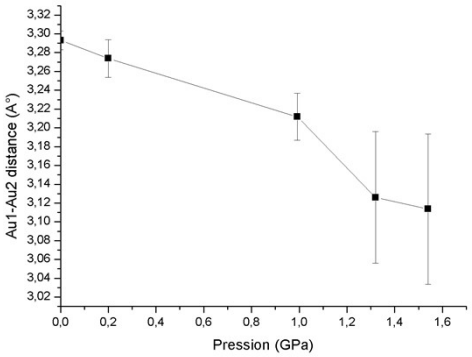


c)

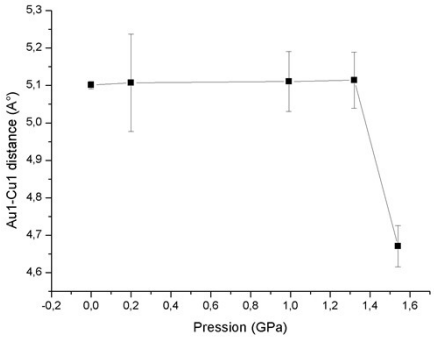
Figure S11: Pressure dependence of cell angles (**a**), cell axes (**b**) and cell volume (**c**).



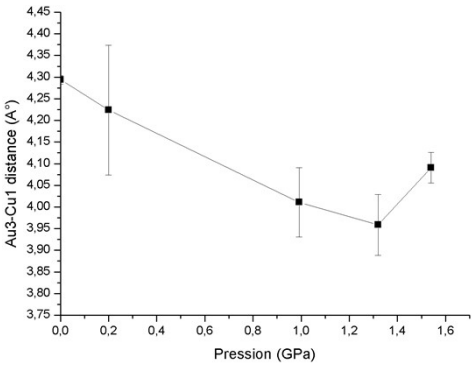
a)



b)



c)



d)

Figure S12: Pressure dependence of the main intermetallic distances and angles (for the error bars, a conservative value of 10 σ has been used as reported in literature).

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	Pressure (GPa)										
Assignement	**0.6**	**0.8**	**1.1**	**1.4**	**1.7**	**2.0**	**2.3**	**2.6**	**2.9**	**3.4**	**3.6**
	94	94									

	110	112	107	106	107	107	107	107	107	107	107
	125	131									
	155	155	155								
	168	170									
	182	182									
	204	204									
γ_{CCC}	236	236									
δ_{AuCN}	248	248									
	256	256									
$\nu_{Cu-N(L1)}$	268	268									
	284										
	300	298									
	305	305									
	318	316									
	366	366			372	372					
$\delta_{CCC} + \nu_{C6-C6}$	371	373	376	377	377	377	380	380	380	383	383
			401	399	398	398	397	397			
$\nu_{Cu-N(C)}$	408	408									
			419	419	423	423	423	423	423	423	423
	436										
ν_{AuCN}	469										
	481										
	(497)	498	499	500	501	501					
	543	544									
γ_{CCC}	551	552									
	635	635									
	642	642									
	648	648									
γ_{CCC}	663	663	663	663	663	663	663	663	663	667	667
					733	733	733	733	733	735	735
	739										
δ_{CCC}	768	768	770	770	772	772	773	773	775	775	775
$\gamma_{CH} + \gamma_{CCC}$	810	810									
γ_{CH}	883	883	884	886	888	888	892	892	892	892	892
δ_{CCC}	958	959									
	(1015)				1015	1016	1016	1018	1018	1020	1020
	1025	1026	1027	1028	1028	1029	1030	1031	1031	1032	1033
ν_{CC}	1035	1035	1035	1036	1038	1038	1039	1040	1041	1044	1044
ν_{CC}	1064	1064	1064	1064	1065	1065	1065	1066	1066	1069	1069
	1088	1088									
$\delta_{CH} + \nu_{CC}$	1108	1109									
	1158	1160									
δ_{CH}	1180	1177	1177	1177	1177	1177	1177	1177	1177	1180	1180
δ_{CH}	1257	1257									
	1271	1271	1271								
ν_{CC}	1286	1282	1282	1282	1282	1282	1286	1286	1286	1289	1289

Table S21: vibrational modes assignement of **1** and dependence from pressure. Frequencies are in cm^{-1}.

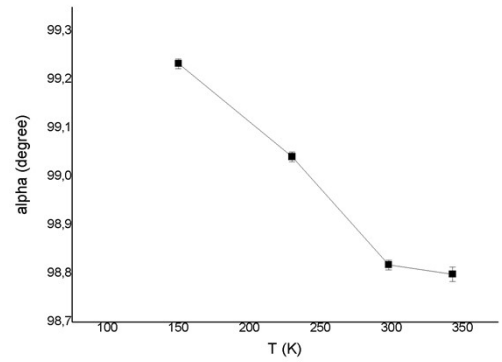
Part 4: Variable temperature SCXRD Measurements on 1 and 6.

Identification code	**1 (T =150 K)**	**1 (T= 230 K)**	**1 (T= 298 K)**	**1 (T= 343 K)**
Empirical formula	$C_{24}H_{16}Au_2CuN_8$	$C_{24}H_{16}Au_2CuN_8$	$C_{24}H_{16}Au_2CuN_8$	$C_{24}H_{16}Au_2CuN_8$
Formula weight	873.92	873.92	873.92	873.92
Temperature/K	150	230.00	293(2)	343(5)
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1	P-1
a/Å	9.9382(3)	9.9530(3)	9.9841(3)	9.9689(3)
b/Å	10.9997(3)	11.0325(3)	11.0973(2)	11.1085(4)
c/Å	12.2677(3)	12.3018(4)	12.3344(3)	12.3564(4)
α/°	99.233(2)	99.041(2)	98.818(2)	98.799(3)
β/°	106.193(2)	106.260(3)	106.224(2)	106.251(3)
γ/°	100.783(2)	100.966(2)	101.345(2)	101.677(3)
Volume/Å^3	1232.57(6)	1240.98(6)	1254.67(5)	1254.11(8)
Z	2	2	2	2
ρ_{calc}g/cm^3	2.355	2.339	2.313	2.314
μ/mm^{-1}	12.758	12.671	12.533	12.538
F(000)	806.0	806.0	806.0	806.0
Crystal size/mm^3	0.35 × 0.22 × 0.21	0.35 × 0.22 × 0.21	0.35 × 0.22 × 0.21	0.35 × 0.22 × 0.21
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.548 to 52.736	3.538 to 52.744	6.52 to 50.06	7.01 to 61.016

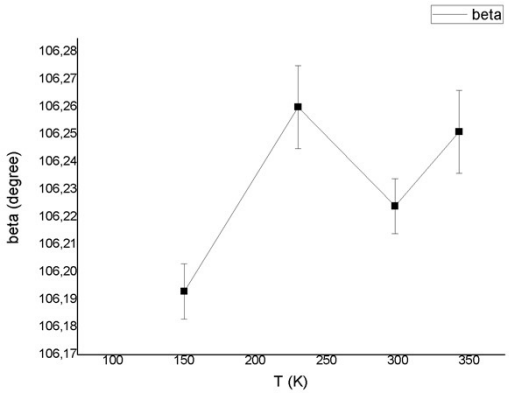
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 12, -15 ≤ l ≤ 15	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	11170	13756	18190	69157
Independent reflections	5040 [R_{int} = 0.0266, R_{sigma} = 0.0284]	5083 [R_{int} = 0.0301, R_{sigma} = 0.0283]	4418 [R_{int} = 0.0324, R_{sigma} = 0.0124]	7640 [R_{int} = 0.0768, R_{sigma} = 0.0378]
Data/restraints/ parameters	5040/0/319	5083/0/319	4418/0/319	7640/0/320
Goodness-of-fit on F^2	1.044	1.044	1.078	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0454, wR_2 = 0.1224	R_1 = 0.0356, wR_2 = 0.0864	R_1 = 0.0214, wR_2 = 0.0542	R_1 = 0.0364, wR_2 = 0.0654
Final R indexes [all data]	R_1 = 0.0514, wR_2 = 0.1268	R_1 = 0.0422, wR_2 = 0.0904	R_1 = 0.0519, wR_2 = 0.0783	R_1 = 0.0619, wR_2 = 0.0733
Largest diff. peak/hole / e $Å^{-3}$	2.25/-0.93	1.40/-1.51	1.20/-0.85	1.10/-0.82

Table S22 Crystal data and structure refinement for **1** at the different temperature**.**

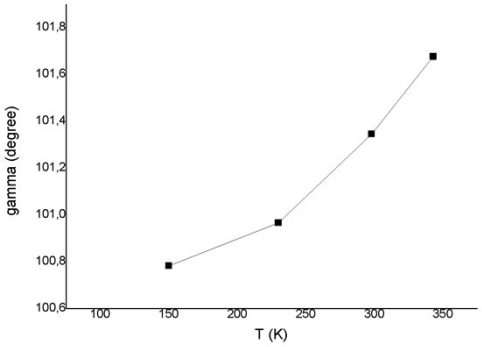
Figure S13: Asymmetric unit of **1.**



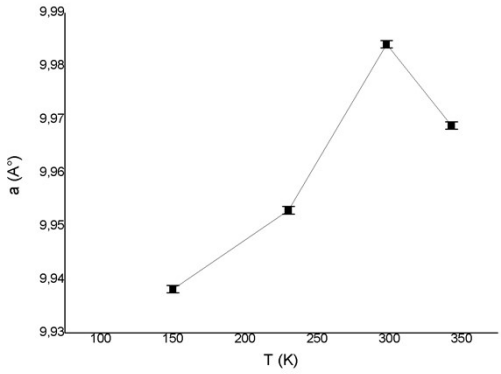
a)



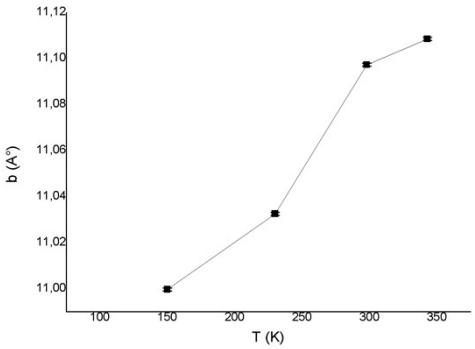
b)



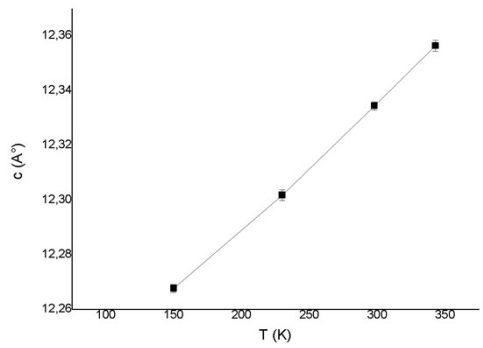
c)



d)

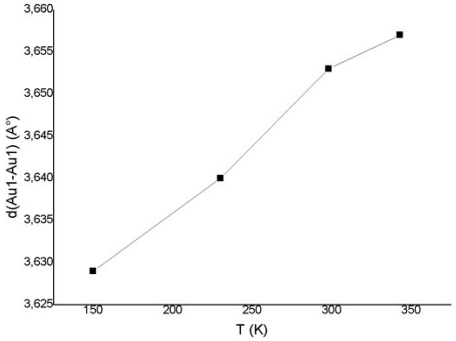


e)

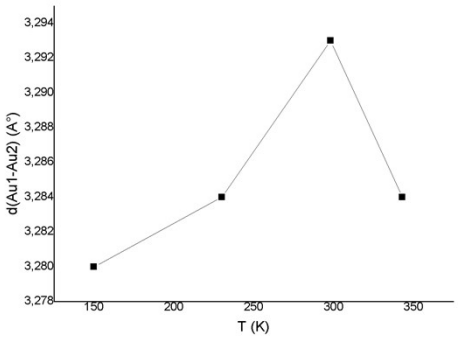


f)

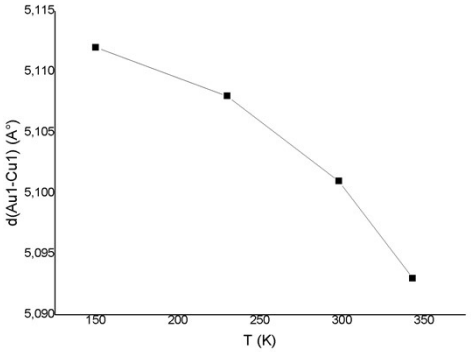
Figure S14: Temperature dependence of cell angles (**a**-**c**) and cell axes (**d**-**f**) for **1** (for the error bars, a conservative value of 10 σ has been used as reported in literature).


d(Au1-Au1) (A°)
3,660
3,655
3,650
3,645
3,640
3,635
3,630
3,625
150
200
250
300
350
T (K)

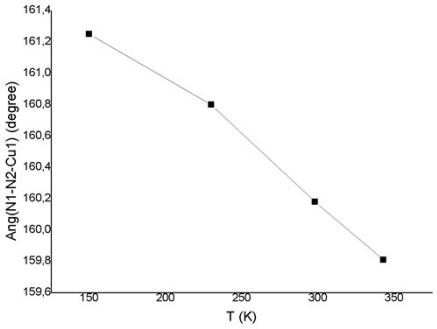
a)


d(Au1-Au2) (A°)
3,294
3,292
3,290
3,288
3,286
3,284
3,282
3,280
3,278
150
200
250
300
350
T (K)

b)

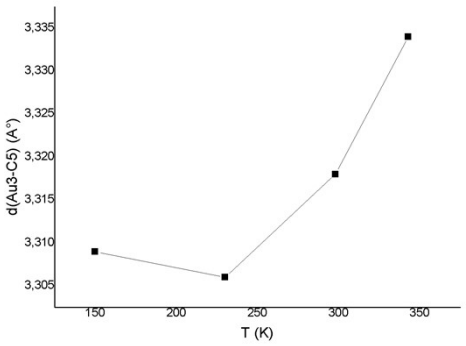

d(Au1-Cu1) (A°)
5,115
5,110
5,105
5,100
5,095
5,090
150
200
250
300
350
T (K)

c)

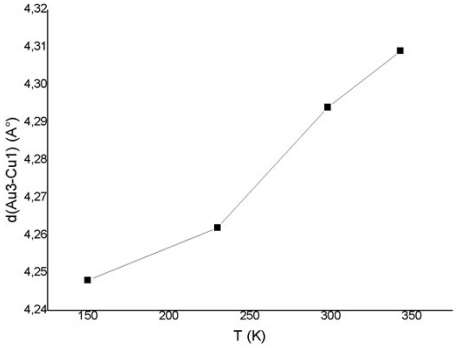

Ang(N1-N2-Cu1) (degree)
161,4
161,2
161,0
160,8
160,6
160,4
160,2
160,0
159,8
159,6
150
200
250
300
350
T (K)

d)

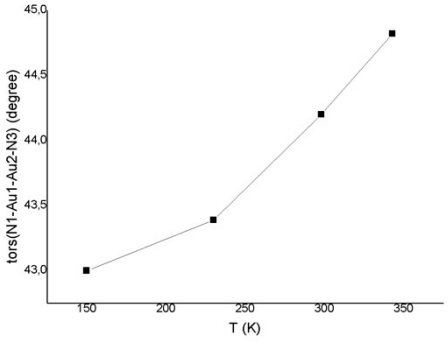
.


d(Au3-C5) (A°)
3,335
3,330
3,325
3,320
3,315
3,310
3,305
150
200
250
300
350
T (K)

e)

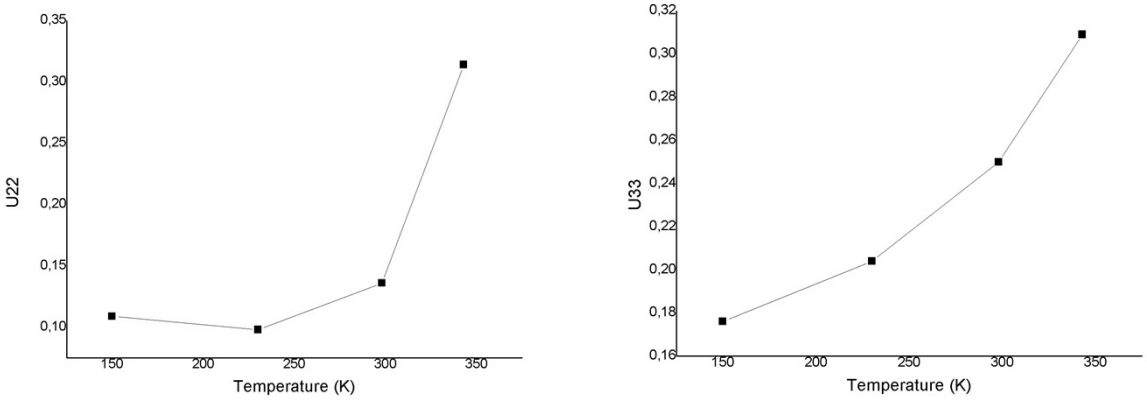

d(Au3-Cu1) (A°)
4,32
4,31
4,30
4,29
4,28
4,27
4,26
4,25
4,24
150
200
250
300
350
T (K)

f)


tors(N1-Au1-Au2-N3) (degree)
45,0
44,5
44,0
43,5
43,0
150
200
250
300
350
T (K)

g)

Figure S15: Temperature dependence of the main distances and angles for **1** (for the error bars, a conservative value of 10 σ has been used as reported in literature).



a) b)

Figure S16: Temperature dependence of U22 and U33 tensor component of N3 atom for **1**.

Identification code	**6 (T= 200K)**	**6 (T= 298K)**	**6 (T= 343K)**
Empirical formula	$C_{28}H_{16}Au_2CuHg_2N_{12}$	$C_{28}H_{16}Au_2CuHg_2N_{12}$	$C_{28}H_{16}Au_2CuHg_2N_{12}$
Formula weight	1379.20	1379.20	1379.18
Temperature/K	200.00	293(2)	342.9(7)
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	Ibam	Ibam	Ibam
a/Å	7.7326(2)	7.7626(13)	7.8055(7)
b/Å	18.2993(6)	18.272(2)	18.3374(16)
c/Å	22.0376(6)	22.003(3)	22.0881(17)
α/°	90	90.00	90
β/°	90	90.00	90
γ/°	90	90.00	90
Volume/Å^3	3118.35(16)	3120.9(8)	3161.5(5)
Z	4	4	4
ρ_{calc}g/cm^3	2.938	2.935	2.898
μ/mm^{-1}	19.901	19.885	19.629
F(000)	2460.0	2460.0	2460.0
Crystal size/mm^3	0.34 × 0.32 × 0.22	0.34 × 0.32 × 0.22	0.34 × 0.32 × 0.24
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.696 to 52.728	6.768 to 52.722	6.768 to 52.722
Index ranges	-9 ≤ h ≤ 9, -22 ≤ k ≤ 22, -27 ≤ l ≤ 27	-7 ≤ h ≤ 9, -17 ≤ k ≤ 21, -23 ≤ l ≤ 26	-9 ≤ h ≤ 9, -22 ≤ k ≤ 21, -27 ≤ l ≤ 21
Reflections collected	16425	6835	16520
Independent reflections	1641 [R_{int} = 0.0850, R_{sigma} = 0.0308]	1421 [R_{int} = 0.0588, R_{sigma} = 0.0308]	1663 [R_{int} = 0.1068, R_{sigma} = 0.0484]

Data/restraints/parameters	1641/73/121	1421/65/121	1663/0/125
Goodness-of-fit on F^2	1.160	1.099	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.0783	R_1 = 0.0358, wR_2 = 0.0756	R_1 = 0.0380, wR_2 = 0.0744
Final R indexes [all data]	R_1 = 0.0470, wR_2 = 0.0814	R_1 = 0.0478, wR_2 = 0.0814	R_1 = 0.0592, wR_2 = 0.0818
Largest diff. peak/hole / e $Å^{-3}$	1.99/-1.36	1.71/-1.28	1.25/-0.97

Table S23 Crystal data and structure refinement for **6** at the different temperature**.**

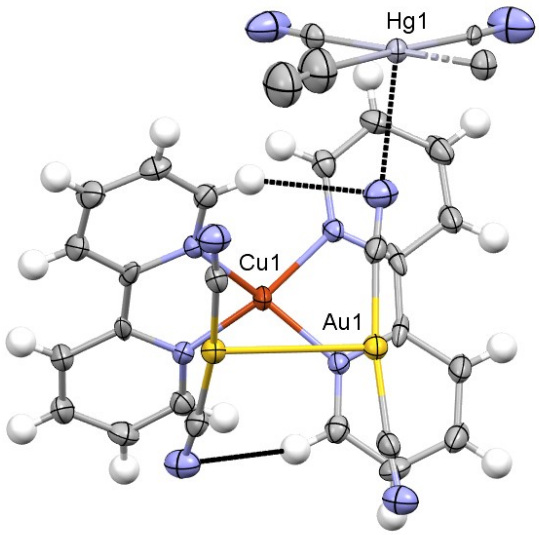
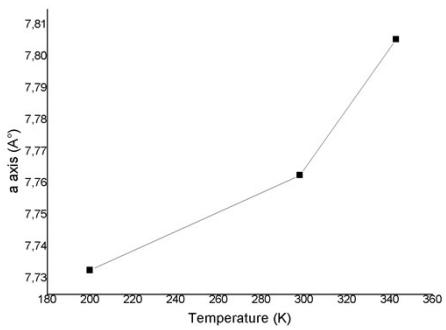
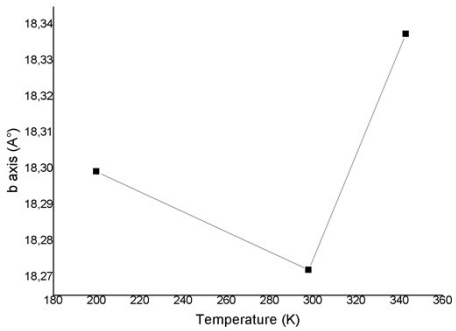


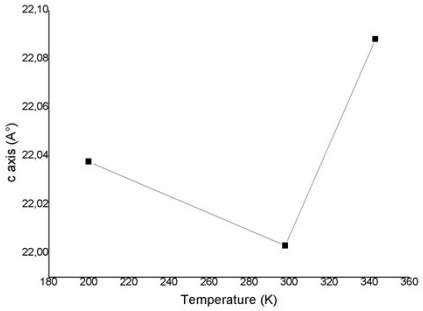
Figure S17: Model of **6** with the numeration of heavy metal atoms for clarity.



a)

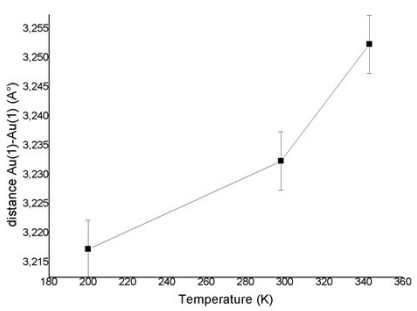


b)

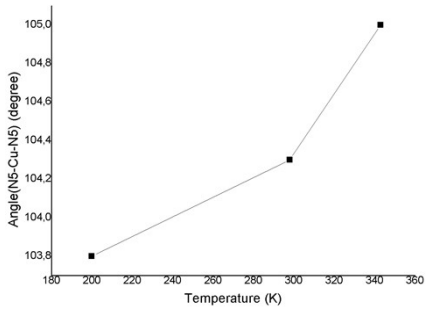


c)

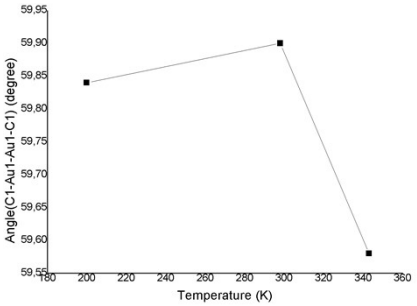
Figure S18: Temperature dependence of cell axes (**a**-**c**) for **6** (for the error bars, a conservative value of 10 σ has been used as reported in literature).



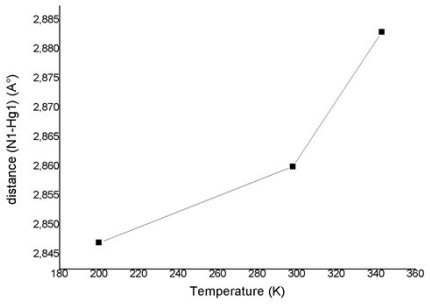
a)



b)



c)



d)

Figure S19: Temperature dependence of the main distances and angles for **6** (for the error bars, a conservative value of 10 σ has been used as reported in literature).