Supplementary Material

Table S1. Crystallographic parameters and data collection details.

Identification code	**1Cl (RT)**	**1Cl (260K)**
Empirical formula	$(C_{12}\ H_{10}\ S_6\ N_2)\ (Au\ Cl_2)_{0.94}$	
Formula weight	625.70	
Temperature	293(2) K	260(2) K
Wavelength	0.71073 Å (Mo Kα)	1.54178 Å (Cu Kα)
Crystal system	Tetragonal	
Space Group	*I-42d*	
Unit cell dimensions	a = 7.3260(1) Å, α = 90º	a = 7.3066 (1) Å, α = 90º
	b = 7.3260(1) Å, β = 90º	b = 7.30660 (1) Å, β = 90º
	c = 67.5487(12) Å, γ = 90 º	c = 67.3719 (12) Å, γ = 90º
Volume	3625.3(1) Å ^{3}	3596.7(1)
Z	8	
Calculated density	2.293 mg/m^3	2.31 mg/m^3
Absorption coefficient	8.577 mm^{-1}	23.504
F(000)	2384	
Crystal size	0.63 × 0.50 × 0.06mm	
Theta range for data collection	3.16 to 27.47°	6.89 to 64.92°
Limiting indices	$-7 \le h \le 7$, $-8 \le k \le 9$, $-68 \le l \le 87$	$-4 \le h \le 7$, $-8 \le k \le 8$, $-76 \le l \le 78$
Reflections collected/unique	5696/2058 [R(int) = 0.0355]	11949/1526[R(int) = 0.0481]
Completeness to theta 27.47	98.4%	98.7%
Absorption correction	Empirical	Numerical
Max. and min. transmission	0.6271 and 0.0994	1.0000 and 0.0288
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2058/1/115	1526/1/114
Goodness-of-fit on F^2	1.067	1.113
Final R indices [$I > 2$sigma(I)]	$R1$ = 0.0441, wR2 = 0.1031 [a]	$R1$ = 0.0455, wR2 = 0.1090 [a]
R indices (all data)	$R1$ = 0.0501, wR2 = 0.1075 [a]	$R1$ = 0.0490, wR2 = 0.1110 [a]
Absolute structure parameter	0.53(2)	0.49(4)
Largest diff. peak and hole	1.661 and −1.984 e Å $^{-3}$	1.530 and −2.344 e Å $^{-3}$

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = ((\max F_o^2, 0) + 2F_c^2)/3$; a = 0.0339, b = 22.02 for **1**Cl(RT) and a = 0.0341, b = 55.02 for **1**Cl(260 K).

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$) for **1**Cl (RT). *U*(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	*y*	*z*	*U*(eq)
Au(1)	**0**	**0**	**0**	**122(1)**
Cl(1)	0	0	344(1)	105(1)
S(1)	−2423(1)	4998(5)	783(1)	35(1)
S(2	−1972(1)	5003(5)	352(1)	33(1)
S(3)	−2007(1)	4998(5)	−124(1)	36(1)
C(1)	−366(15)	2329(9)	976(1)	59(3)
C(2)	−832(8)	4383(8)	979(1)	37(1)
C(3)	−931(6)	4921(17)	583(1)	25(1)
C(4)	0	5000	215(1)	27(1)
C(6)	−949(6)	4975(18)	−355(1)	29(1)
C(5)	0	5000	13(1)	26(1)
N(1)	−1935(5)	4915(16)	−520(1)	38(1)
C(7)	−928(6)	5000(20)	−688(1)	39(1)
Au(2)	5000	5000	1255(1)	398(12)
Cl(2)	5053(14)	1890(20)	1268(3)	143(16)

Table S3. Bond lengths [Å] and angles [°] for **1**Cl (RT).

Au(1)-Cl(1)$^{\#1}$	2.323(4)
Au(1)-Cl(1)	2.323(4)
S(1)-C(3)	1.742(4)
S(1)-C(2)	1.818(6)
S(2)-C(4)	1.717(3)
S(2)-C(3)	1.735(4)
S(3)-C(5)	1.736(3)
S(3)-C(6)	1.746(4)
C(1)-C(2)	1.543(9)
C(1)-H(1A)	0.96
C(1)-H(1B)	0.96
C(1)-H(1C)	0.96
C(2)-C(2)$^{\#2}$	1.518(12)
C(2)-H(2)	0.98
C(3)-C(3)$^{\#2}$	1.369(9)
C(4)-C(5)	1.365(6)
C(4)-S(2)$^{\#2}$	1.717(3)
C(6)-N(1)	1.327(5)
C(6)-C(6)$^{\#2}$	1.390(8)
C(5)-S(3)$^{\#2}$	1.736(3)
N(1)-C(7)	1.355(6)
C(7)-C(7)$^{\#2}$	1.359(9)
C(7)-H(7)	0.93
C(3)-S(1)-C(2)	98.9(3)

Table S3. *Cont.*

C(4)-S(2)-C(3)	96.6(2)
C(5)-S(3)-C(6)	95.7(2)
C(2)#2-C(2)-C(1)	113.8(7)
C(2)$^{\#2}$-C(2)-S(1)	111.6(4)
C(1)-C(2)-S(1)	112.0(5)
C(2)$^{\#2}$-C(2)-H(2)	106.3
C(3)$^{\#2}$-C(3)-S(2)	115.78(19)
C(3)$^{\#2}$-C(3)-S(1)	128.5(2)
S(2)-C(3)-S(1)	114.9(2)
C(5)-C(4)-S(2)	122.73(14)
C(5)-C(4)-S(2)$^{\#2}$	122.74(14)
S(2)-C(4)-S(2)$^{\#2}$	114.5(3)
N(1)-C(6)-C(6)$^{\#2}$	123.1(3)
N(1)-C(6)-S(3)	120.6(3)
C(6)$^{\#2}$-C(6)-S(3)	116.35(14)
C(4)-C(5)-S(3)$^{\#2}$	122.11(15)
C(4)-C(5)-S(3)	122.11(15)
S(3)$^{\#2}$-C(5)-S(3)	115.8(3)
C(6)-N(1)-C(7)	113.8(4)
N(1)-C(7)-C(7)$^{\#2}$	123.0(3)
N(1)-C(7)-H(7)	118.5
C(7)$^{\#2}$-C(7)-H(7)	118.5

Symmetry transformations used to generate equivalent atoms: #1 −*y*, *x*,-z; #2 -*x*, −*y* + 1, *z*.

Table S4. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 ×10^3) for **1**Cl (260 K). *U*(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

x	*y*	*z*	*U*(eq)	*x*
Au(1)	0	0	0	102(1)
Cl(1)	0	0	341(1)	91(1)
S(1)	−2429(2)	499665)	784(1)	24(1)
S(2)	−1978(2)	5003(6)	353(1)	23(1)
S(3)	−2012(2)	5006(6)	−124(1)	26(1)
C(1)	−414(15)	2327(12)	980(1)	39(3)
C(2)	−833(11)	4378(20)	980(1)	30(2)
C(3)	−942(8)	4970(20)	584(1)	16(1)
C(4)	0	5000	215(1)	20(2)
C(6)	−948(8)	4960(20)	−356(1)	18(1)
C(5)	0	5000	12(1)	18(1)
N(1)	−1933(7)	4940(19)	−522(1)	28(1)
C(7)	−937(9)	4990(30)	−688(1)	28(1)
Au(2)	5000	5000	1254(1)	364(16)
Cl(2)	5060(20)	1870(20)	1263(3)	110(20)

Table S5. Bond lengths [Å] and angles [°] for **1**Cl (260 K).

Au(1)-Cl(1)$^{\#1}$	2.296(5)
Au(1)-Cl(1)	2.296(5)
S(1)-C(3)	1.735(5)
S(1)-C(2)	1.825(7)
S(2)-C(4)	1.721(3)
S(2)-C(3)	1.722(4)
S(3)-C(5)	1.732(4)
S(3)-C(6)	1.742(4)
C(1)-C(2)	1.533(11)
C(2)-C(2)$^{\#2}$	1.518(15)
C(3)-C(3)$^{\#2}$	1.391(10)
C(4)-C(5)	1.362(8)
C(4)-S(2)$^{\#2}$	1.721(3)
C(6)-N(1)	1.333(6)
C(6)-C(6)$^{\#2}$	1.390(10)
C(5)-S(3)$^{\#2}$	1.732(4)
N(1)-C(7)	1.338(7)
C(7)-C(7)$^{\#2}$	1.358(11)
C(3)-S(1)-C(2)	99.7(3)
C(4)-S(2)-C(3)	97.1(2)
C(5)-S(3)-C(6)	95.5(2)
C(2)$^{\#2}$-C(2)-C(1)	114.7(8)
C(2)$^{\#2}$-C(2)-S(1)	111.4(5)
C(1)-C(2)-S(1)	111.5(5)
C(3)$^{\#2}$-C(3)-S(2)	115.76(19)
C(3)$^{\#2}$-C(3)-S(1)	128.41(19)
S(2)-C(3)-S(1)	115.7(3)
C(5)-C(4)-S(2)$^{\#2}$	122.89(17)
C(5)-C(4)-S(2)	122.90(17)
S(2)$^{\#2}$-C(4)-S(2)	114.2(3)
N(1)-C(6)-C(6)$^{\#2}$	122.6(3)
N(1)-C(6)-S(3)	121.0(4)
C(6)$^{\#2}$-C(6)-S(3)	116.42(17)
C(4)-C(5)-S(3)	121.93(18)
C(4)-C(5)-S(3)$^{\#2}$	121.93(18)
S(3)-C(5)-S(3)$^{\#2}$	116.1(4)
C(6)-N(1)-C(7)	114.1(5)
N(1)-C(7)-C(7)$^{\#2}$	123.2(3)

Symmetry transformations used to generate equivalent atoms: #1 $-y$, x, $-z$; #2 $-x$, $-y+1$, z.

Figure S1. Numbering scheme, S···S and S···N contacts of donor molecules. Symmetry transformations used to generate equivalent atoms: (’): −*x*, 1 − *y*, z; (’’): -*y*, 1 + *x*, −*z*; (’’ ’) : −1 + *x*,1 = *x*, −*z*.