Supplementary Material (ESI) for CrystEngComm

SUPPORTING INFORMATION

Nuclearity control in gold dithiocarboxylato compounds

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Instrumentation

Electronic absorption spectra of solutions in carbon disulfide of 3.30, 1.65 and 0.83 mg/mL (*ca.* 10, 5 and 2.5 mM) were recorded on an Agilent 8452 diode array spectrophotometer over a 190–1100 nm range in 0.1 cm quartz cuvettes thermostated by an Unisoku cryostat.

Mass spectra were recorded in MALDI-TOF, reflector positive, with DCTB matrix of a carbon disulfide solution. Bruker ULTRAFLEX III TOF TOF spectrophotometer with a Nd:YAG laser (λ= 355 nm).

Elemental analysis was carried out by a LECO CHNS-932 analyzer.

^{1}H and DOSY NMR spectra were recorded at different temperatures (298K, 273K and 240 K) on a Bruker 600 MHz AVANCE spectrometer equipped with a 5 mm TBI probe. The sample used contained a 5 mg/mL solution of compound **1** in a mixture 3:1 $CS_2/CDCl_3$. DOSY experiments were recorded using the DSTE pulse sequence with a diffusion time (Δ) of 150 ms. Sine-shaped pulsed-field gradients with a duration of 1.5 ms (δ) followed by a recovery delay of 100 μs were incremented from 2 to 95% of the maximum strength in 16 equally spaced steps. Diffusion coefficients were extracted directly from the DOSY spectra. They were automatically calculated by the DOSY tool included in the TOPSPIN software package v2.1 (from Bruker Biospin). Diffusion values are obtained by measuring the slope in the following linear relationship: $\ln(A_g/A_o)=-\gamma^2 g^2 \delta^2(4\Delta - \delta)D$; where A_g and A_o are the signal intensities in the presence and absence of pulsed field gradient (PFG), respectively, γ is the gyromagnetic ratio (radsg^{-1}), g is the strength of the diffusion gradients (Gcm^{-1}), D is the diffusion coefficient of the observed spins (m^{2}s^{-1}), δ is the length of the diffusion gradient (s), and Δ is the time separation between the leading edges of the two diffusion pulsed gradients (s). All chemical shifts values (δ) are given in ppm.

Synthesis of the compounds

*Compound **1**:* A solution of isopentanedithio acid (72 mg, 0.54 mmol) in ethanol (2 mL) was slowly added to a solution of $KAu(CN)_2$ (33 mg, 0.11 mmol) in ethanol (4 mL). After one day at room temperature, the solution was concentrated to 3.5 mL and kept overnight at 7 ºC. Afterwards, the solid was filtered, washed with diethyl ether (2×10 mL) and dried under vacuum (21 mg, 58 % yield) $C_{10}H_{18}Au_2S_4$: Found: C, 17.4; H, 2.7; S, 19.2. Calc. for $C_{10}H_{18}Au_2S_4$: C, 18.2; H, 2.75; S, 19.4 %. δ (500 MHz; 303 K;

$CDCl_3/CS_2$ 1:3; $SiMe_4$) 1.11-1.13 (3.5 H, d, J 6.5, CH_3CHCH_2), 2.30-2.38 (0.59 H, m, CH_3CHCH_2), 2.87 (1 H, d, J 7.0, CH_3CHCH_2) and 2.94 (0.16 H, d, J 7.0, CH_3CHCH_2). δ (500 MHz; 223 K; $CDCl_3/CS_2$ 1:3; $SiMe_4$) 1.06-1.10 (11.25 H, 3d, J 6.5, CH_3CHCH_2), 2.28-2.34 (1.82 H, m, CH_3CHCH_2), 2.82 (1 H, d, J 7.5, CH_3CHCH_2) and 2.87-2.91 (2.77 H, 2d, J 7.5, CH_3CHCH_2). m/z (MALDI, DCTB): 659.9 $[Au_2(C_5H_9S_2)_2]$, 989.9 $[Au_3(C_5H_9S_2)_3]$, 1319. 9 $[Au_4(C_5H_9S_2)_4]$, 1186.9 $[Au_4(C_5H_9S_2)_3]$, 1131.2 {$[Au_4(C_5H_9S_2)_3(CHS_2)]$ 1130.8 + $[Au_4(C_5H_9S_2)_3(CH_2S_2)]$ 1131.9}, 1516.9 $[Au_5C_5H_9S_2)_4]$, 1461.2 {$[Au_5(C_5H_9S_2)_4(CHS_2)]$ 1460.8 + $[Au_5(C_5H_9S_2)_4(CH_2S_2)]$ 1461.8}. The purity of the crystal samples has been checked by powder X-ray diffraction (Figure S3).

Compound **2** was obtained by slow vapour diffusion of diethyl ether on a solution of **1** (6 mg) in carbon disulfide (2 mL) at 7 ºC. The crystals formed were filtered, washed with diethyl ether and in air (4 mg, 67 % yield). $C_{10}H_{18}Au_2S_4$: Found: C, 17.2; H, 2.7; S, 19.3. Calc. for $C_{10}H_{18}Au_2S_4$: C, 18.2; H, 2.75; S, 19.4 %. δ (500 MHz; 298 K; $CDCl_3/CS_2$ 1:3; $SiMe_4$) 1.11-1.13 (3.5 H, d, J 6.5, CH_3CHCH_2), 2.30-2.38 (0.59 H, m, CH_3CHCH_2), 2.87 (1 H, d, J 7.0, CH_3CHCH_2) and 2.94 (0.16 H, d, J 7.0, CH_3CHCH_2).

Crystallographic data

Crystal data were collected on a Xcalibur diffractometer equipped with an area detector and graphite monochromated MoKα radiation (λ = 0.71073 Å). All structures were solved by direct methods using the SIR92 program[1] and refined by full matrix least-squares on *F*2 including all reflections (SHELXL97).[2] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in geometrically calculated positions and refined with isotropically according to the riding model. Selected bond distances and angles of the structures of compounds **1** and **2** are presented in Table S1 and Table S2 respectively. Crystal data, data collection and refinement parameters for compounds **1** and **2** are summarized in Table S3.

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[1] A. Altomare, M. Cascarano, C.Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343–350.

[2] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Goettingen, Germany, 1993

Table S1: Selected Bond Distances (Å) and Angles (deg) for compound **1**.

Au1-S1	2.303(3)	S1-Au1-S1^{i}	180.00(-)
Au1-S1^{i}	2.303(3)	S2-Au2-S3	169.37(10)
Au2-S2	2.306(3)	S4-Au3-S5	161.76(10)
Au2-S3	2.294(3)	S6-Au4-S7	175.85(10)
Au3-S4	2.304(3)	S8-Au5-S9	157.66(10)
Au3-S5	2.296(3)	S10-Au6-S10^{ii}	180.00(-)
Au4-S6	2.301(3)	S11-Au7-S12^{iii}	174.94(11)
Au4-S7	2.298(3)	S13-Au8-S14^{iv}	174.70(11)
Au5-S8	2.288(3)		
Au5-S9	2.291(3)		
Au6-S10	2.288(3)		
Au6-S10^{ii}	2.288(3)		
Au7-S11	2.297(3)		
Au7-S12^{iii}	2.296(3)		
Au8-S13	2.282(4)		
Au8-S14^{iv}	2.296(4)		
Au1···Au2	2.9157(4)	Au2-Au1-Au2^{i}	180.00(-)
Au1···Au2^{i}	2.9157(4)	Au1-Au2-Au3	139.957(17)
Au2···Au3	2.9658(6)	Au2-Au3-Au4	72.783(16)
Au3···Au4	3.0327(6)	Au2-Au3-Au7	72.968(15)
Au3···Au7	3.2910(6)	Au4-Au3-Au7	140.682(19)
Au4···Au5	3.0576(6)	Au3-Au4-Au5	145.833(19)
Au5···Au6	3.0246(4)	Au6-Au5-Au4	76.170(13)
Au5···Au8	3.3892(6)	Au6-Au5-Au8	66.511(12)
Au7···Au7^{iii}	2.8838(8)	Au4-Au5-Au8	139.221(18)
Au8···Au8^{iv}	2.8737(9)	Au5-Au6-Au5^{ii}	180.00(-)
		Au3-Au7-Au7^{iii}	175.06(3)
		Au5-Au8-Au8^{iv}	174.42(3)

Symmetry codes: (i) 2–x, –y, 1–z; (ii) 2–x, –y, 2–z; (iii) 1–x, –y, 1–z; (iv) 3–x, –y, 2–z.

Table S2: Selected Bond Distances (Å) and Angles (deg) for compound **2**.

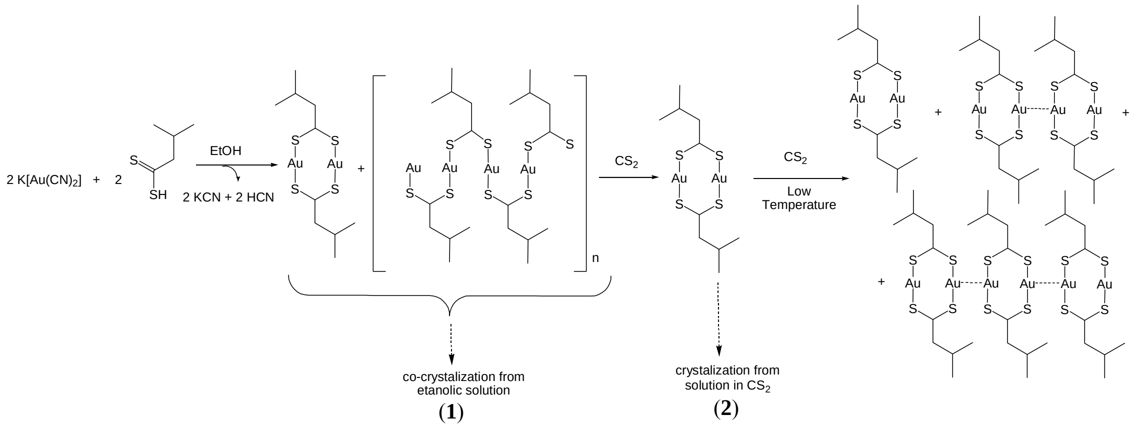
Au1-S1	2.306(3)	S1-Au1-S2^{i}	172.27(10)
Au1-S2^{i}	2.306(3)	S3-Au2-S5	173.63(12)
Au2-S3	2.306(3)	S4-Au3-S6	173.94(12)
Au2-S5	2.313(3)	S7-Au4-S8^{ii}	170.53(11)
Au3-S4	2.305(3)	S9-Au5-S11	173.30(10)
Au3-S6	2.311(3)	S10-Au6-S12	175.50(10)
Au4-S7	2.303(4)	S13-Au7-S15	173.17(12)
Au4-S8^{ii}	2.310(4)	S14-Au8-S16	175.21(10)
Au5-S9	2.281(3)	S17-Au9-S18^{iii}	172.72(12)
Au5-S11	2.286(3)		
Au6-S10	2.308(3)		
Au7-S13	2.299(3)		
Au7-S15	2.307(3)		
Au8-S14	2.292(3)		
Au8-S16	2.295(3)		
Au9-S17	2.302(3)		
Au9-S18^{iii}	2.307(3)		
Au1···Au1^{i}	2.8003(9)	Au1^{i}-Au1-Au2	140.50(3)
Au1···Au2	2.9387(6)	Au3-Au2-Au9	120.51(2)
Au2···Au3	2.8054(7)	Au3-Au2-Au1	116.21(2)
Au2···Au9	2.9246(6)	Au9-Au2-Au1	123.01(2)
Au3···Au4	3.1167(7)	Au2-Au3-Au4	149.38(2)
Au3···Au6	3.3304(6)	Au2-Au3-Au6^{ii}	94.577(18)
Au4···Au4^{ii}	2.8180(10)	Au4-Au3-Au6^{ii}	59.895(15)
Au4···Au6^{ii}	3.2238(7)	Au4^{ii}-Au4-Au3	144.16(3)
Au5···Au6	2.8420(6)	Au4^{ii}-Au4-Au6^{ii}	95.78(2)
Au5···Au7	3.0021(6)	Au3-Au4-Au6^{ii}	63.346(15)
Au7···Au8	2.8427(6)	Au6-Au5-Au7	166.77(2)
Au9···Au9^{iii}	2.7986(9)	Au5-Au6-Au4^{ii}	112.507(19)
		Au5-Au6-Au3^{ii}	165.668(19)
		Au4^{ii}-Au6-Au3^{ii}	56.759(14)
		Au8-Au7-Au5	165.97(3)
		Au9^{iii}-Au9-Au2	140.51(3)

Symmetry codes: (i) –x, –y, –z; (ii) –x, –y, –1–z; (iii) 1–x, –y, –z.

Table S3: Crystallographic data for compounds **1** and **2**.[a]

	1	**2**
Formula	$C_{35} H_{63} Au_7 S_{14}$	$C_{10} H_{18} Au_2 S_4$
CCDC	758809	758808
Formula weight (g mol^{-1})	2311.46	660.42
Crystal color and habit	red trapezoids	black plates
Crystal size (mm)	0.16×0.09×0.03	0.29×0.20×0.08
Crystal system	triclinic	triclinic
Space group	P-*1*	P-*1*
Unit cell dimensions		
a (Å)	9.2796(5)	15.3128(6)
b (Å)	15.4914(9)	16.0078(9)
c (Å)	18.8044(11)	16.1656(8)
α (°)	85.919(5)	113.203(5)
β (°)	81.923(4)	100.270(4)
γ (°)	87.427(4)	95.062(4)
V (Å^3)	2667.9(3)	3528.3(3)
Z	2	9
T (K)	100(2)	100(2)
λ (Å)	0.71069	0.71069
D_{calcd}, (g cm^{-3})	2.877	2.797
μ (Mo Kα) (mm^{-1})	19.745	19.196
$F(000)$	2100	2700
θ range (°)	2.79 - 27.14	2.99 - 28.00
No. independent reflections	11428	16916
No. reflections observed $I > 2\sigma(I)$	6685	11084
No. parameters refined	522	649
R_1 (obs. data)	0.0385	0.0454
wR_2 (obs. data)	0.0686	0.1011
R_1 (all data)	0.0802	0.0832
wR_2 (all data)	0.0727	0.1069
Goodness-of-fit, S	0.801	1.036
Residual ρ_{max}, ρ_{min} (e Å^{-3})	2.579, -1.602	4.738, -2.266

[a] $R1=\Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR2=[\Sigma w(||Fo| - |Fc||)^2/\Sigma w|Fo|^2]^{1/2}$.



Scheme S1. Scheme of the reaction and transformation processes taking place.

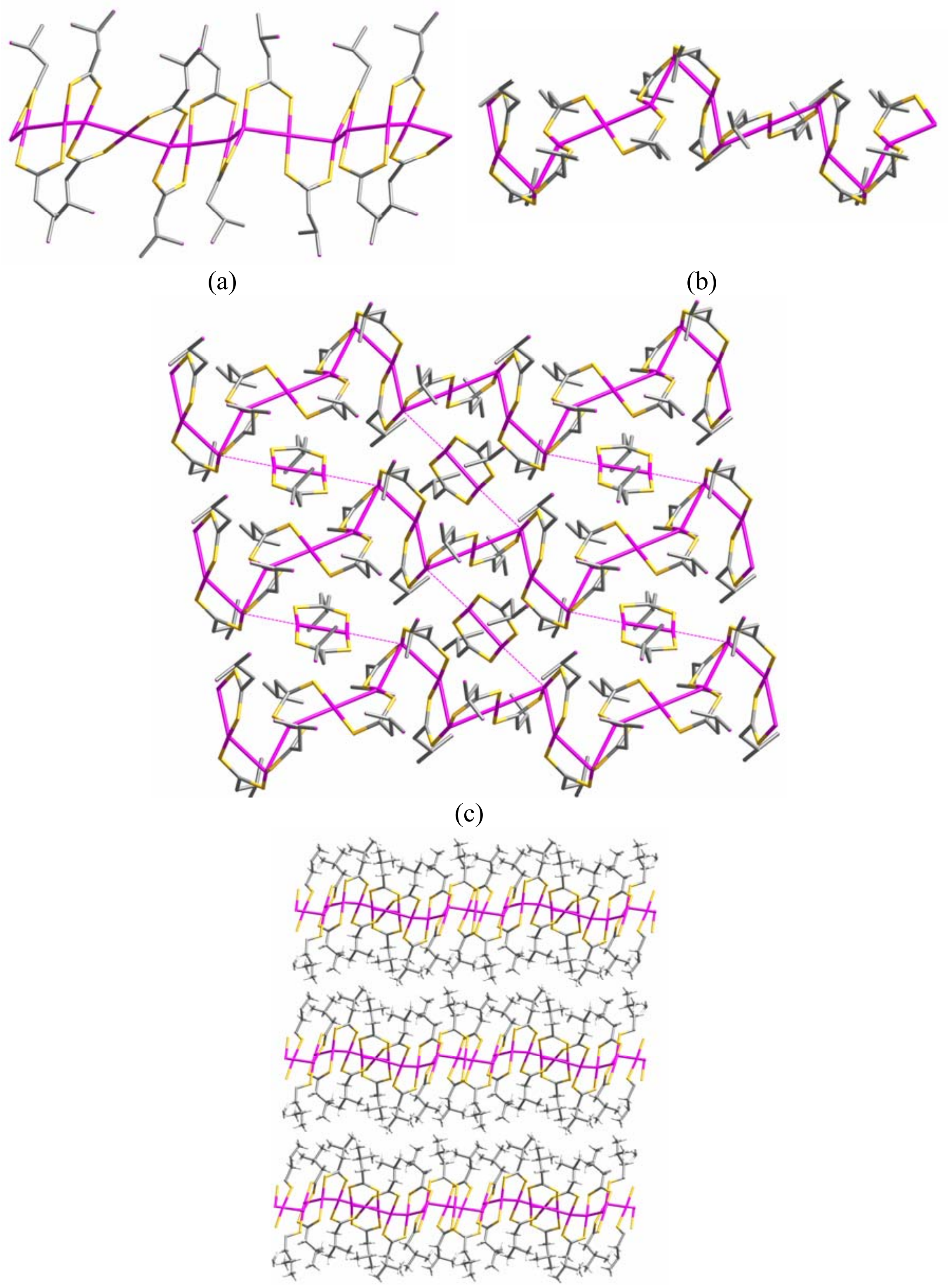
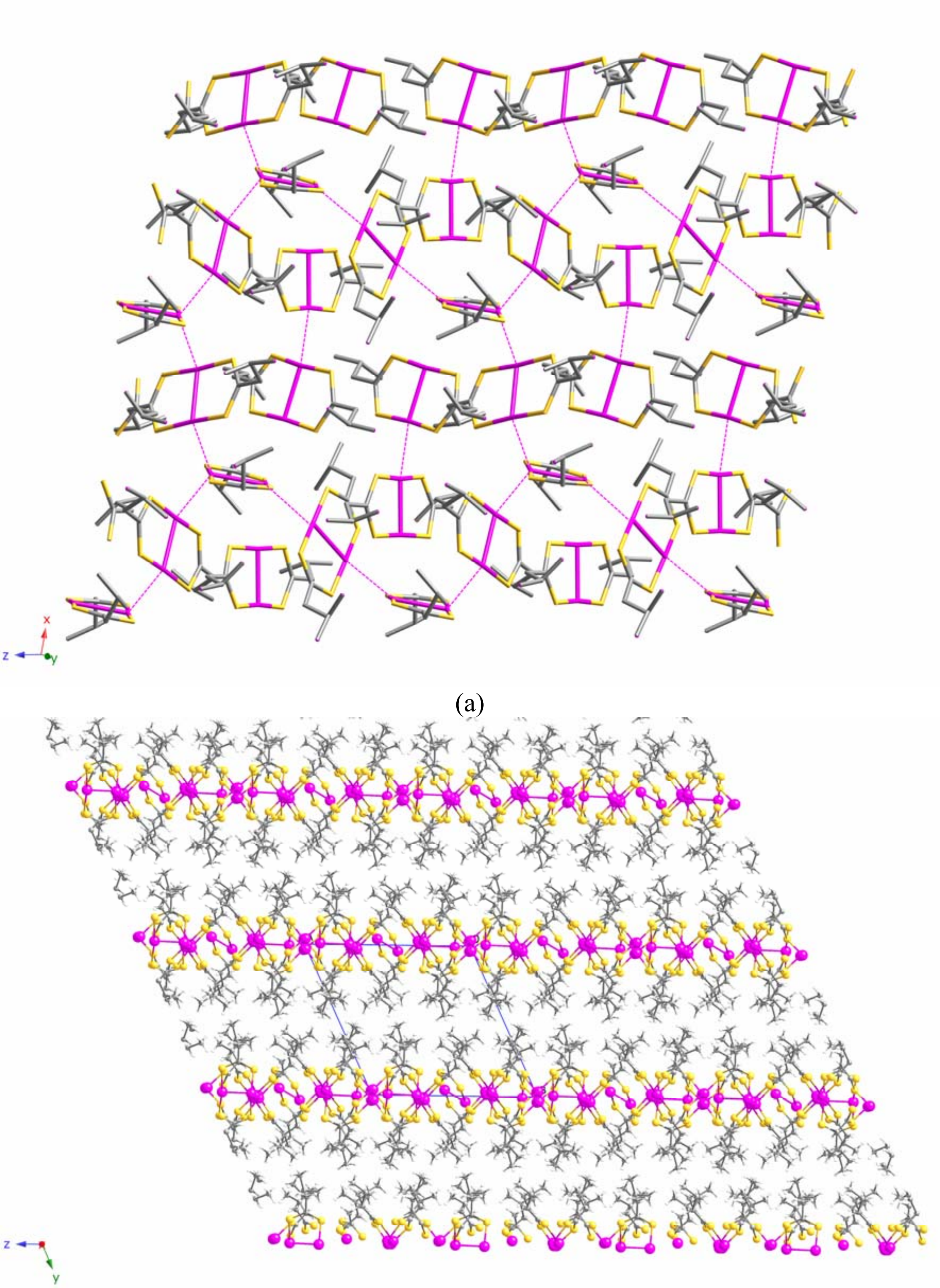


Figure S1. Crystal packing of compound **1**: (a) and (b) views of the dithiocarboxylate-gold chain. (c) Supramolecular layer of gold chains and gold dimers held together by means of aurophilic interactions (dashed lines: intermolecular Au···Au contacts) and (d) pile up of the supramolecular layers through weak van der Waals interactions among the aliphatic residues.



(a)

(b)

Figure S2. Crystal packing of compound **2**: (a) Supramolecular layer of gold dimers held together by means of aurophilic interactions (dashed lines: intermolecular Au···Au contacts) and (b) pile up of the supramolecular layers through weak van der Waals interactions among the aliphatic residues.

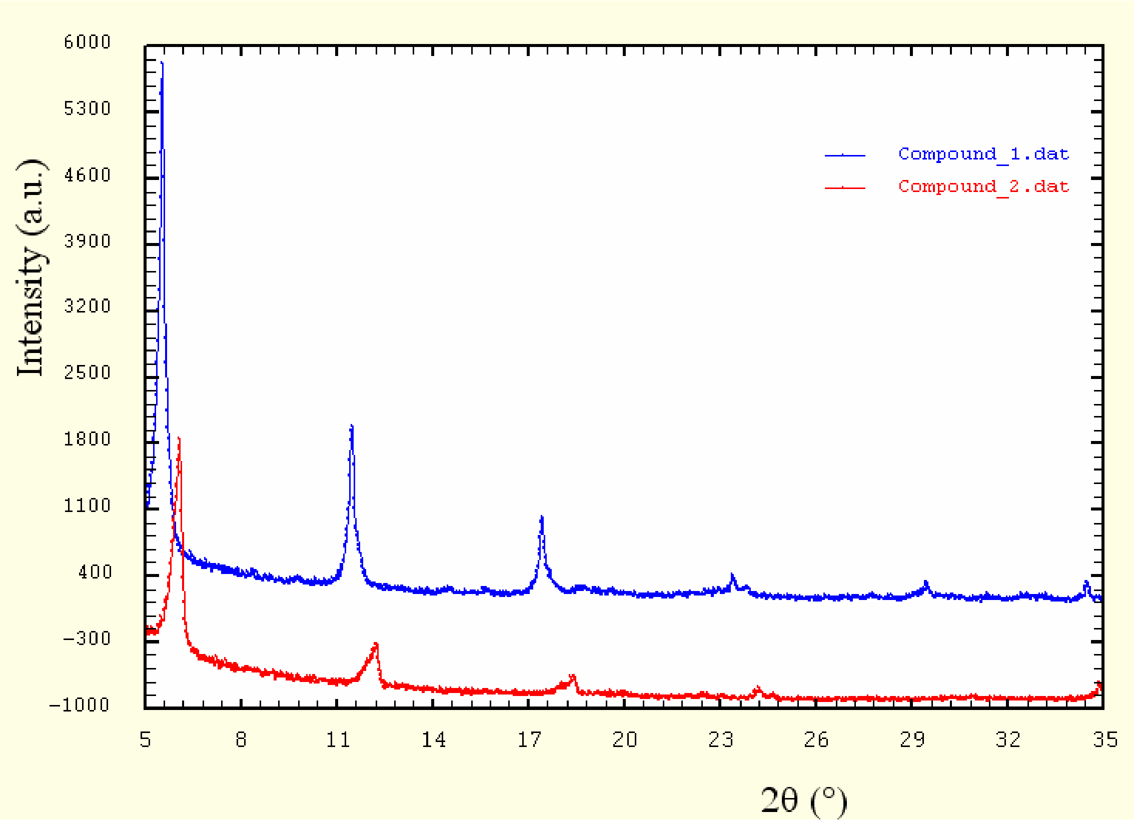


Figure S3. XRPD diagrams of compounds **1** and **2**.