Supplementary Material (ESI) for CrystEngComm

Electronic supplementary information (ESI)

Dimensionality of coordination polymers decided by the type of hybridization of the central carbon atom of the solvent molecule that coordinates to an alkali metal cation: from discrete to 3D networks based on a gold(III) bis(dithiolene) complex †

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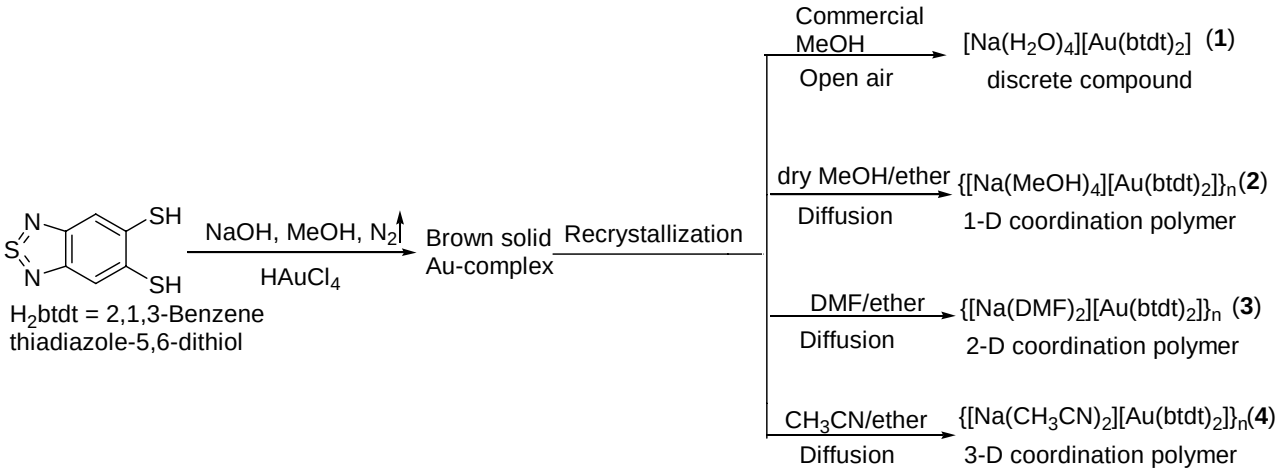
A. Experimental section



H_2btdt = 2,1,3-Benzene thiadiazole-5,6-dithiol

Scheme S1 Synthetic route for compounds **1-4.**

Materials: The material $HAuCl_4.3H_2O$ was purchased from Finar Reagents. The solvents were distilled and dried by standard procedures. The H_2btdt ligand was prepared according to literature procedure.[1]

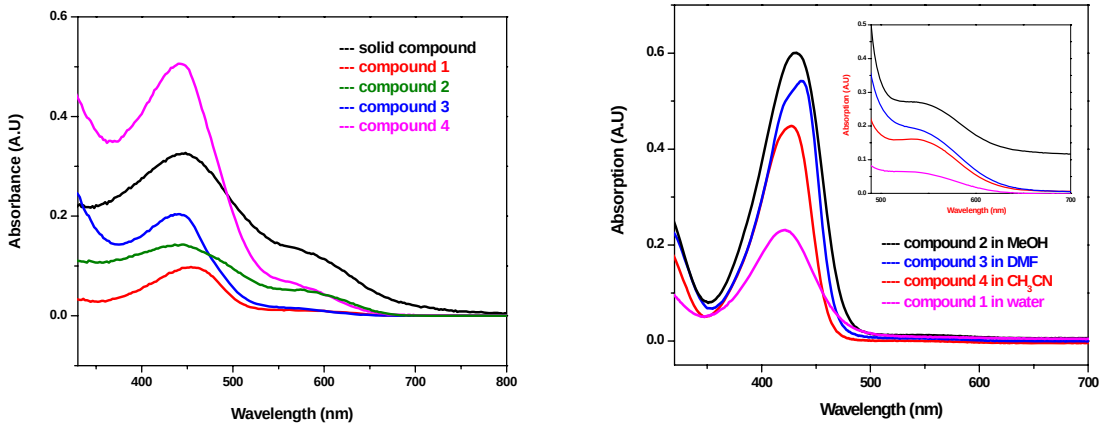
Reference

1 J. L. Brusso, O. P. Clements, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed and J. F. Richardson, *J. Am. Chem. Soc.*, 2004, **126**, 8256.

Instrumental methods: FLASH EA series 1112 CHNS analyzer performed elemental analyses. Infrared spectra were recorded as KBr pellets on a JASCO–5300 FT–IR spectrophotometer at 298K. Electronic absorption spectra of solutions were recorded on a Cary 100 Bio UV-Vis spectrophotometer. Diffused reflectance spectra of solid compounds were recorded on a UV-3600 Shimadzu UV-Vis-NIR spectrophotometer.

B. Spectroscopy

1. Electronic Absorption spectra



(a) (b)

Fig. S1 (a) The diffuse reflectance spectra of compounds **1-4** and brown solid compound. (b) Absorption spectra of compounds **1-4** from their corresponding solvents.

2. IR spectroscopy

IR spectrum compound **3** and **4** show characteristic bands at 1657 cm^{-1}(C=O stretching frequency) and 2255 cm^{-1} (C≡N stretching frequency) respectively.

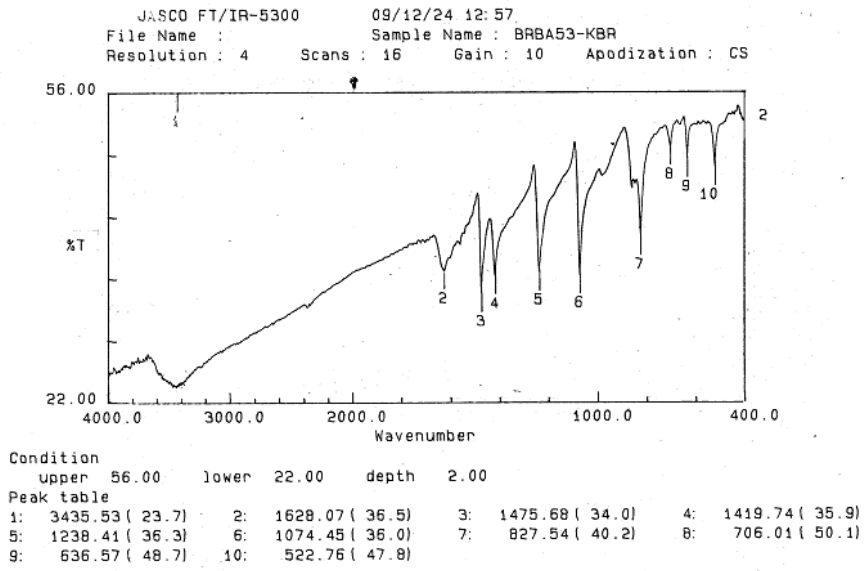


Fig. S2 IR spectrum of brown solid compound.

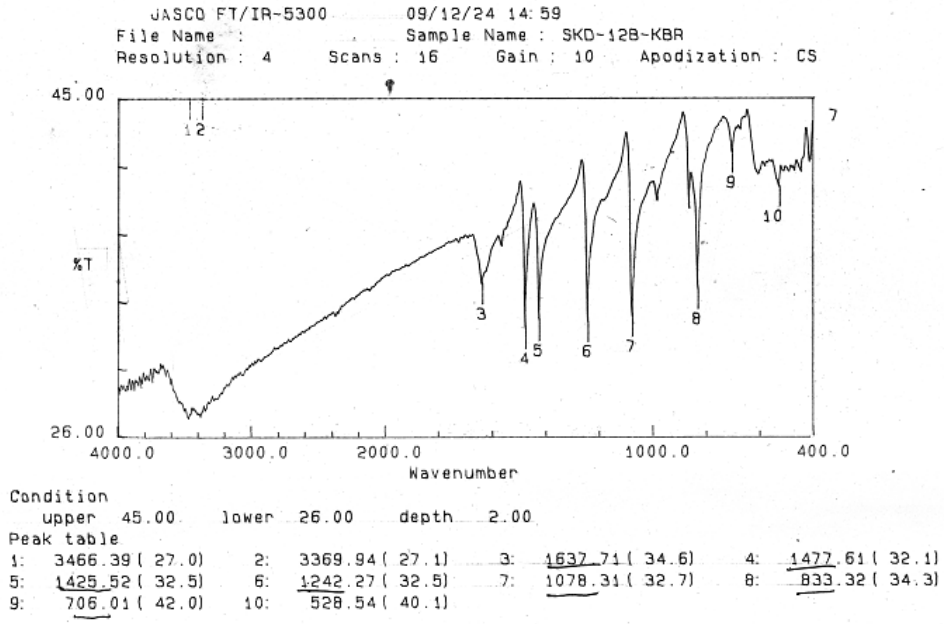


Fig. S3 IR spectrum of compound $[Na(H_2O)_4][Au(btdt)_2]$ (**1**).

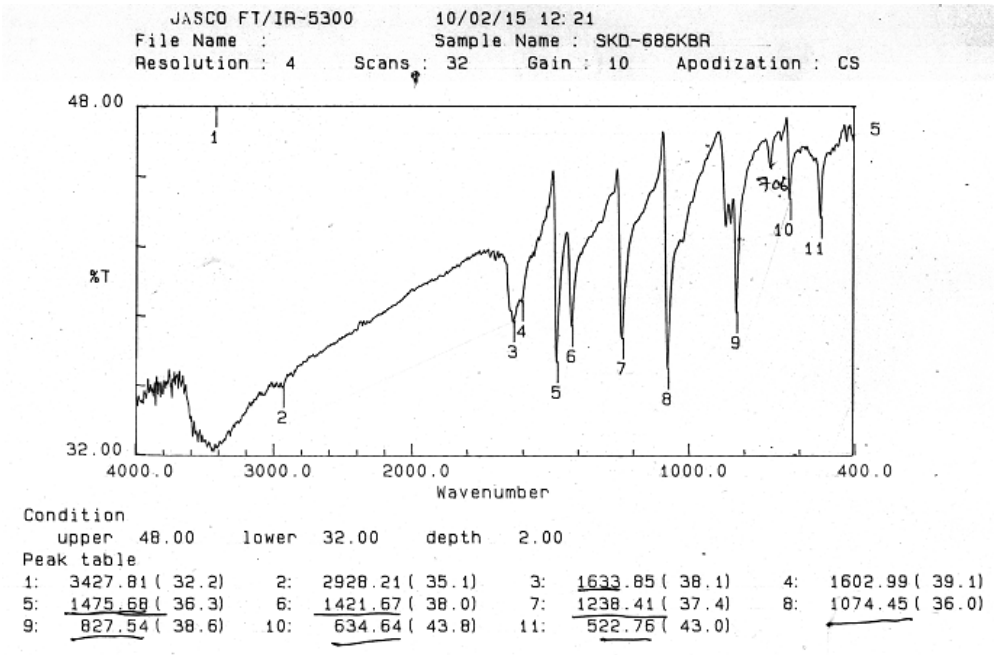


Fig. S4 IR spectrum of compound $\{[Na(MeOH)_4][Au(btdt)_2]\}_n$ (**2**).

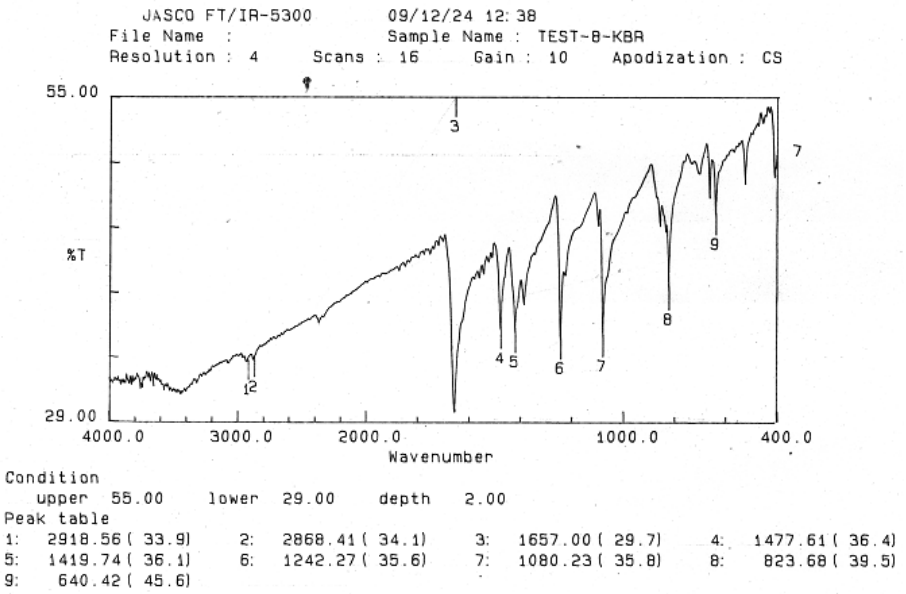


Fig. S5 IR spectrum of compound $\{[Na(DMF)_2][Au(btdt)_2]\}_n$ (**3**).

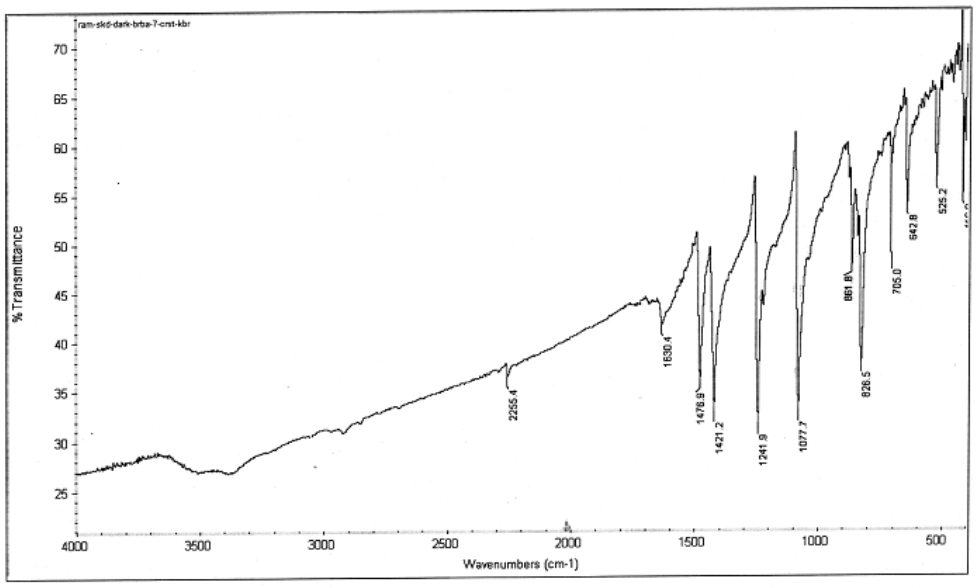


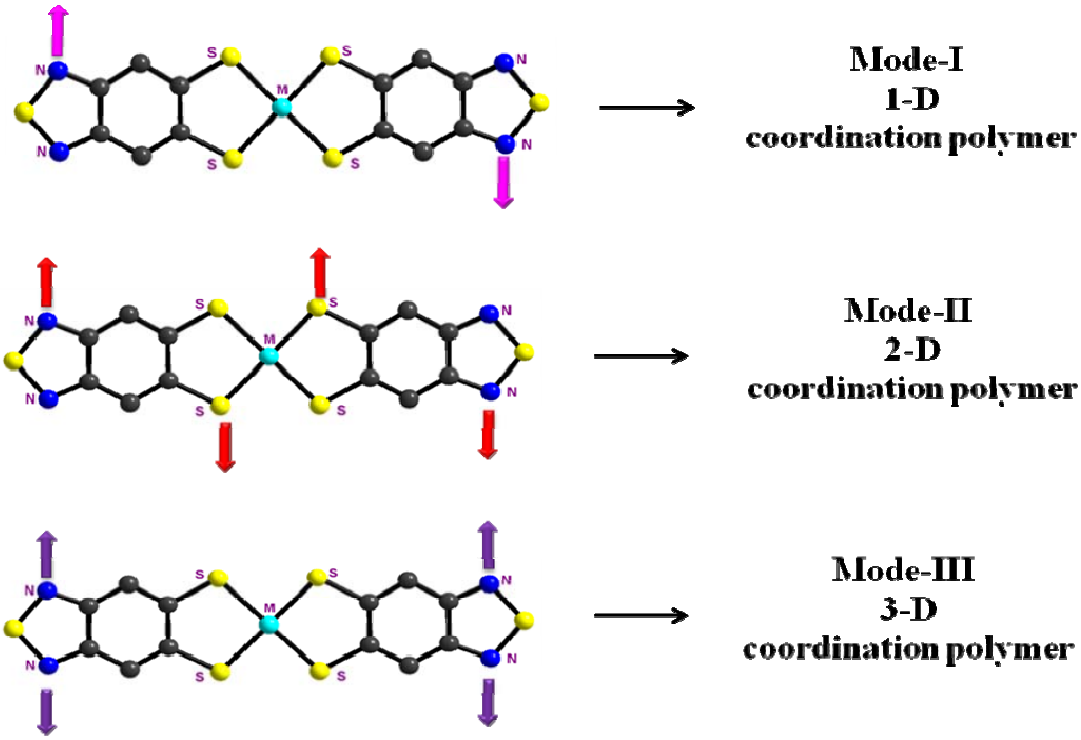
Fig. S6 IR spectrum of compound $\{[Na(CH_3CN)_2][Au(btdt)_2]\}_n$ (**4**).

C. X-ray Crystallography

Crystal data for compound **1** was collected on Oxford XCalibur, Gemini diffractometer equipped with EOS CCD detector at 298 K. Monochromatic Mo Kα radiation (0.71073 Å) was used for the measurements. Absorption corrections using multi ψ-scans were applied. Structure was solved using SHELXS-97, and refined by full-matrix least squares against F^2 using SHELXL-97 software [36]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Selected bond lengths and angles for compound **1** are listed in Table S1.

Crystal data for compounds **2-4** were measured at 100(2) K on a Bruker SMART APEX CCD area detector system [λ(Mo-Kα) = 0.71073 Å], graphite monochromator, 2400 frames were recorded with an ω scan width of 0.3°, each for 8 s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction by SAINTPLUS (Software for the CCD Detector System,

Bruker Analytical X-Ray Systems Inc., Madison, WI, 1998), structure solution using SHELXS-97 (G. M. Sheldrick, Program for structure solution, University of Göttingen, Germany 1997) and refined using SHELXL-97 (G. M. Sheldrick, Program for crystal structure analysis, University of Göttingen, Germany 1997). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculation by using a riding model. Selected bond lengths and angles for the compounds **2-4** are listed in Table S2, Table S3 and Table S4, respectively.



Scheme S2 The observed coordination modes of Na^{+} ion with $[Au(btdt)_2]^{-}$ in the compounds **2–4.**

Table S1 Selected bond lengths [Å] and angles [°] for compound **1**.

Au(1)-S(2)	2.3090(15)	C(9)-N(4)	1.359(7)
Au(1)-S(4)	2.3100(14)	C(9)-C(10)	1.433(8)
Au(1)-S(3)	2.3174(15)	C(10)-N(3)	1.363(6)
Au(1)-S(1)	2.3176(15)	C(10)-C(11)	1.399(8)
C(1)-C(2)	1.369(7)	C(11)-C(12)	1.382(7)
C(1)-C(6)	1.434(7)	C(12)-S(3)	1.761(5)
C(1)-S(2)	1.765(5)	N(1)-S(5)	1.623(5)
C(2)-C(3)	1.421(7)	N(2)-S(5)	1.616(5)
C(3)-N(1)	1.345(6)	N(3)-S(6)	1.628(5)
C(3)-C(4)	1.403(7)	N(4)-S(6)	1.632(5)
C(4)-N(2)	1.357(6)	Na(1)-O(1)	2.282(5)
C(4)-C(5)	1.438(7)	Na(1)-O(3)	2.335(6)
C(5)-C(6)	1.379(7)	Na(1)-O(2)	2.384(6)
C(6)-S(1)	1.761(5)	Na(1)-O(4)	2.415(5)
C(7)-C(8)	1.367(7)	Na(1)-O(4)#1	2.422(5)
C(7)-C(12)	1.426(7)	Na(1)-Na(1)#1	3.282(5)
C(7)-S(4)	1.765(5)	O(4)-Na(1)#1	2.422(5)
C(8)-C(9)	1.421(7)		

S(2)-Au(1)-S(4)	177.85(6)	N(4)-C(9)-C(8)	125.8(5)
S(2)-Au(1)-S(3)	90.17(5)	N(4)-C(9)-C(10)	114.2(5)
S(4)-Au(1)-S(3)	89.62(5)	C(8)-C(9)-C(10)	119.9(5)
S(2)-Au(1)-S(1)	89.60(5)	N(3)-C(10)-C(11)	126.5(5)
S(4)-Au(1)-S(1)	90.60(5)	N(3)-C(10)-C(9)	112.9(5)
S(3)-Au(1)-S(1)	179.57(6)	C(11)-C(10)-C(9)	120.6(5)
C(2)-C(1)-C(6)	121.1(5)	C(12)-C(11)-C(10)	118.4(5)
C(2)-C(1)-S(2)	117.7(4)	C(11)-C(12)-C(7)	121.2(5)
C(6)-C(1)-S(2)	121.2(4)	C(11)-C(12)-S(3)	117.4(4)
C(1)-C(2)-C(3)	117.9(5)	C(7)-C(12)-S(3)	121.4(4)
N(1)-C(3)-C(4)	113.4(5)	C(3)-N(1)-S(5)	106.7(4)
N(1)-C(3)-C(2)	125.6(5)	C(4)-N(2)-S(5)	106.2(4)
C(4)-C(3)-C(2)	121.1(5)	C(10)-N(3)-S(6)	106.1(4)
N(2)-C(4)-C(3)	113.7(5)	C(9)-N(4)-S(6)	105.4(4)
N(2)-C(4)-C(5)	125.2(5)	O(1)-Na(1)-O(3)	90.9(2)
C(3)-C(4)-C(5)	121.1(5)	O(1)-Na(1)-O(2)	96.0(2)
C(6)-C(5)-C(4)	116.4(5)	O(3)-Na(1)-O(2)	162.0(2)
C(5)-C(6)-C(1)	122.3(5)	O(1)-Na(1)-O(4)	168.0(2)
C(5)-C(6)-S(1)	116.5(4)	O(3)-Na(1)-O(4)	88.2(2)
C(1)-C(6)-S(1)	121.2(4)	O(2)-Na(1)-O(4)	81.64(19)
C(8)-C(7)-C(12)	121.4(5)	O(1)-Na(1)-O(4)#1	97.20(18)
C(8)-C(7)-S(4)	117.3(4)	O(3)-Na(1)-O(4)#1	105.4(2)
C(12)-C(7)-S(4)	121.3(4)	O(2)-Na(1)-O(4)#1	90.31(19)
C(7)-C(8)-C(9)	118.4(5)	O(4)-Na(1)-O(4)#1	94.56(17)

O(1)-Na(1)-Na(1)#1	144.3(2)	C(6)-S(1)-Au(1)	103.91(18)
O(3)-Na(1)-Na(1)#1	99.9(2)	C(1)-S(2)-Au(1)	103.97(18)
O(2)-Na(1)-Na(1)#1	84.09(16)	C(12)-S(3)-Au(1)	103.65(18)
O(4)-Na(1)-Na(1)#1	47.37(13)	C(7)-S(4)-Au(1)	103.77(18)
O(4)#1-Na(1)-Na(1)#1	47.19(13)	N(2)-S(5)-N(1)	100.0(2)
Na(1)-O(4)-Na(1)#1	85.44(17)	N(3)-S(6)-N(4)	101.3(2)

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

Table S2 Selected bond lengths [Å] and angles [°] for compound **2**.

Au(1)-S(2)#1	2.3085(6)	C(1)-C(2)	1.441(3)
Au(1)-S(2)	2.3085(6)	C(6)-C(5)	1.417(3)
Au(1)-S(1)#1	2.3085(6)	C(5)-C(4)	1.430(3)
Au(1)-S(1)	2.3085(6)	C(4)-C(3)	1.417(3)
S(3)-N(1)	1.621(2)	C(3)-C(2)	1.376(3)
S(3)-N(2)	1.627(2)	O(1)-C(7)	1.423(3)
S(1)-C(1)	1.761(2)	O(1)-Na(1)	2.3479(18)
S(2)-C(2)	1.767(2)	O(2)-C(8)	1.427(3)
N(1)-C(5)	1.346(3)	O(2)-Na(1)	2.3511(19)
N(1)-Na(1)	2.518(2)	Na(1)-O(1)#2	2.3479(18)
N(2)-C(4)	1.347(3)	Na(1)-O(2)#2	2.3511(19)
C(1)-C(6)	1.374(3)	Na(1)-N(1)#2	2.518(2)
S(2)#1-Au(1)-S(2)	180.0	N(1)-C(5)-C(4)	113.4(2)
S(2)#1-Au(1)-S(1)#1	90.01(2)	C(6)-C(5)-C(4)	120.4(2)
S(2)-Au(1)-S(1)#1	89.99(2)	N(2)-C(4)-C(3)	126.4(2)
S(2)#1-Au(1)-S(1)	89.99(2)	N(2)-C(4)-C(5)	113.1(2)
S(2)-Au(1)-S(1)	90.01(2)	C(3)-C(4)-C(5)	120.5(2)
S(1)#1-Au(1)-S(1)	179.999(1)	C(2)-C(3)-C(4)	118.2(2)
N(1)-S(3)-N(2)	100.29(11)	C(3)-C(2)-C(1)	121.3(2)
C(1)-S(1)-Au(1)	103.82(8)	C(3)-C(2)-S(2)	117.75(18)
C(2)-S(2)-Au(1)	103.88(8)	C(1)-C(2)-S(2)	120.89(17)
C(5)-N(1)-S(3)	106.59(16)	C(7)-O(1)-Na(1)	140.13(17)
C(5)-N(1)-Na(1)	127.01(15)	C(8)-O(2)-Na(1)	122.17(15)
S(3)-N(1)-Na(1)	114.02(10)	O(1)-Na(1)-O(1)#2	180.00(10)
C(4)-N(2)-S(3)	106.59(16)	O(1)-Na(1)-O(2)#2	98.25(7)
C(6)-C(1)-C(2)	121.1(2)	O(1)#2-Na(1)-O(2)#2	81.75(7)
C(6)-C(1)-S(1)	117.48(18)	O(1)-Na(1)-O(2)	81.75(7)
C(2)-C(1)-S(1)	121.39(17)	O(1)#2-Na(1)-O(2)	98.25(7)
C(1)-C(6)-C(5)	118.4(2)	O(2)#2-Na(1)-O(2)	180.0
N(1)-C(5)-C(6)	126.1(2)	O(1)-Na(1)-N(1)	95.58(6)

O(1)#2-Na(1)-N(1)	84.42(6)	O(1)#2-Na(1)-N(1)#2	95.59(6)
O(2)#2-Na(1)-N(1)	85.82(7)	O(2)#2-Na(1)-N(1)#2	94.18(7)
O(2)-Na(1)-N(1)	94.18(7)	O(2)-Na(1)-N(1)#2	85.82(7)
O(1)-Na(1)-N(1)#2	84.41(6)	N(1)-Na(1)-N(1)#2	180.0

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

Table S3 Selected bond lengths [Å] and angles [°] for compound **3**.

Au(1)-S(1)#1	2.3051(7)	C(5)-C(6)	1.404(4)
Au(1)-S(1)	2.3051(7)	C(7)-O(1)	1.232(4)
Au(1)-S(2)	2.3107(7)	C(7)-N(3)	1.320(4)
Au(1)-S(2)#1	2.3107(7)	C(8)-N(3)	1.460(4)
C(1)-C(6)	1.368(4)	C(9)-N(3)	1.449(4)
C(1)-C(2)	1.437(4)	N(1)-S(3)	1.615(2)
C(1)-S(1)	1.765(3)	N(2)-S(3)	1.622(2)
C(2)-C(3)	1.377(4)	N(2)-Na(1)	2.488(2)
C(2)-S(2)	1.761(3)	Na(1)-O(1)#2	2.316(2)
C(3)-C(4)	1.411(4)	Na(1)-O(1)	2.316(2)
C(4)-N(2)	1.349(3)	Na(1)-N(2)#2	2.488(2)
C(4)-C(5)	1.434(4)	Na(1)-S(1)#3	3.2020(8)
C(5)-N(1)	1.344(4)		

S(1)#1-Au(1)-S(1)	179.999(2)	C(1)-C(6)-C(5)	118.5(2)
S(1)#1-Au(1)-S(2)	89.94(2)	O(1)-C(7)-N(3)	125.8(3)
S(1)-Au(1)-S(2)	90.06(2)	C(5)-N(1)-S(3)	106.28(19)
S(1)#1-Au(1)-S(2)#1	90.06(2)	C(4)-N(2)-S(3)	106.23(18)
S(1)-Au(1)-S(2)#1	89.94(2)	C(4)-N(2)-Na(1)	137.23(18)
S(2)-Au(1)-S(2)#1	180.0	S(3)-N(2)-Na(1)	115.70(12)
C(6)-C(1)-C(2)	121.5(2)	C(7)-N(3)-C(9)	121.5(2)
C(6)-C(1)-S(1)	117.2(2)	C(7)-N(3)-C(8)	121.3(2)
C(2)-C(1)-S(1)	121.3(2)	C(9)-N(3)-C(8)	117.2(2)
C(3)-C(2)-C(1)	120.9(2)	O(1)#2-Na(1)-O(1)	180.0
C(3)-C(2)-S(2)	118.1(2)	O(1)#2-Na(1)-N(2)#2	83.55(7)
C(1)-C(2)-S(2)	121.05(19)	O(1)-Na(1)-N(2)#2	96.45(7)
C(2)-C(3)-C(4)	118.3(2)	O(1)#2-Na(1)-N(2)	96.45(7)
N(2)-C(4)-C(3)	126.6(2)	O(1)-Na(1)-N(2)	83.55(7)
N(2)-C(4)-C(5)	112.9(2)	N(2)#2-Na(1)-N(2)	180.00(8)
C(3)-C(4)-C(5)	120.4(2)	O(1)#2-Na(1)-S(1)#3	87.99(6)
N(1)-C(5)-C(6)	126.1(2)	O(1)-Na(1)-S(1)#3	92.01(6)
N(1)-C(5)-C(4)	113.5(2)	N(2)#2-Na(1)-S(1)#3	92.31(5)
C(6)-C(5)-C(4)	120.4(2)	N(2)-Na(1)-S(1)#3	87.69(5)

O(1)#2-Na(1)-S(1)#4	92.01(6)	C(1)-S(1)-Au(1)	103.61(9)
O(1)-Na(1)-S(1)#4	87.99(6)	C(1)-S(1)-Na(1)#5	91.78(9)
N(2)#2-Na(1)-S(1)#4	87.69(5)	Au(1)-S(1)-Na(1)#5	112.42(3)
N(2)-Na(1)-S(1)#4	92.31(5)	C(2)-S(2)-Au(1)	103.75(9)
S(1)#3-Na(1)-S(1)#4	179.999(12)	N(1)-S(3)-N(2)	101.00(12)
C(7)-O(1)-Na(1)	143.47(19)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+2 #2 -x+1,-y,-z+1 #3 -x+1,-y+1,-z+1 #4 x,y-1,z
#5 x,y+1,z

Table S4 Selected bond lengths [Å] and angles [°] for compound **4**.

Au(1)-S(2)#1	2.3033(9)	C(3)-N(1)	1.349(4)
Au(1)-S(2)	2.3033(9)	S(3)-N(2)	1.617(3)
Au(1)-S(1)#1	2.3052(9)	S(3)-N(1)	1.623(3)
Au(1)-S(1)	2.3052(9)	N(2)-Na(1)#2	2.456(3)
S(1)-C(6)	1.761(3)	N(1)-Na(1)	2.542(3)
C(1)-C(2)	1.380(5)	Na(1)-N(3)	2.455(3)
C(1)-C(6)	1.437(4)	Na(1)-N(3)#3	2.455(3)
C(1)-S(2)	1.754(3)	Na(1)-N(2)#4	2.456(3)
C(2)-C(3)	1.407(5)	Na(1)-N(2)#5	2.456(3)
C(6)-C(5)	1.362(4)	Na(1)-N(1)#3	2.542(3)
C(4)-N(2)	1.346(4)	Na(1)-S(3)#3	3.3616(8)
C(4)-C(5)	1.411(4)	N(3)-C(7)	1.138(4)
C(4)-C(3)	1.431(4)	C(7)-C(8)	1.453(5)

S(2)#1-Au(1)-S(2)	180.0	C(5)-C(4)-C(3)	120.6(3)
S(2)#1-Au(1)-S(1)#1	90.03(3)	C(6)-C(5)-C(4)	118.7(3)
S(2)-Au(1)-S(1)#1	89.97(3)	N(1)-C(3)-C(2)	127.1(3)
S(2)#1-Au(1)-S(1)	89.97(3)	N(1)-C(3)-C(4)	113.2(3)
S(2)-Au(1)-S(1)	90.03(3)	C(2)-C(3)-C(4)	119.7(3)
S(1)#1-Au(1)-S(1)	180.0	N(2)-S(3)-N(1)	100.46(14)
C(6)-S(1)-Au(1)	103.42(11)	C(1)-S(2)-Au(1)	103.49(11)
C(2)-C(1)-C(6)	120.7(3)	C(4)-N(2)-S(3)	106.8(2)
C(2)-C(1)-S(2)	118.0(2)	C(4)-N(2)-Na(1)#2	129.5(2)
C(6)-C(1)-S(2)	121.3(2)	S(3)-N(2)-Na(1)#2	121.63(14)
C(1)-C(2)-C(3)	118.9(3)	C(3)-N(1)-S(3)	106.4(2)
C(5)-C(6)-C(1)	121.2(3)	C(3)-N(1)-Na(1)	132.4(2)
C(5)-C(6)-S(1)	117.7(2)	S(3)-N(1)-Na(1)	105.46(13)
C(1)-C(6)-S(1)	121.1(2)	N(3)-Na(1)-N(3)#3	180.0
N(2)-C(4)-C(5)	126.3(3)	N(3)-Na(1)-N(2)#4	95.90(10)
N(2)-C(4)-C(3)	113.1(3)	N(3)#3-Na(1)-N(2)#4	84.10(10)

N(3)-Na(1)-N(2)#5	84.10(10)	N(2)#5-Na(1)-N(1)	92.79(9)
N(3)#3-Na(1)-N(2)#5	95.90(10)	N(1)#3-Na(1)-N(1)	180.0
N(2)#4-Na(1)-N(2)#5	180.0	N(3)-Na(1)-S(3)#3	67.55(7)
N(3)-Na(1)-N(1)#3	88.37(10)	N(3)#3-Na(1)-S(3)#3	112.45(7)
N(3)#3-Na(1)-N(1)#3	91.63(10)	N(2)#4-Na(1)-S(3)#3	112.10(7)
N(2)#4-Na(1)-N(1)#3	92.80(9)	N(2)#5-Na(1)-S(3)#3	67.90(7)
N(2)#5-Na(1)-N(1)#3	87.20(9)	N(1)#3-Na(1)-S(3)#3	27.74(6)
N(3)-Na(1)-N(1)	91.63(10)	N(1)-Na(1)-S(3)#3	152.26(6)
N(3)#3-Na(1)-N(1)	88.37(10)	C(7)-N(3)-Na(1)	152.5(3)
N(2)#4-Na(1)-N(1)	87.20(9)	N(3)-C(7)-C(8)	177.5(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+2 #2 -x+2,y+1/2,-z+3/2 #3 -x+2,-y+1,-z+1 #4 x,-y+3/2,z-1/2
#5 -x+2,y-1/2,-z+3/2